

By the same author

CHEMISTRY IN DAILY LIFE

THE ELECTROCHEMISTRY OF SOLUTIONS

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To V.

PREFACE TO SECOND EDITION

THE excellent reception accorded to the first issue of this book has encouraged the author to follow very much the same lines in the present edition, although the subject matter has been completely revised and brought up to date. The sections dealing with the theory of electrolytic dissociation and with overvoltage have been almost entirely re-written to conform with the latest developments in these subjects. Most of the material originally found in the chapter entitled 'Acids and Bases' has been included in that on 'Equilibria in Electrolytes', and the treatment of ionic product and hydrolysis, together with a general discussion of acid, base and solvent equilibria, has been incorporated in a new chapter. The author has found the modern viewpoint concerning acids and bases very illuminating, and its advantages should be more widely realized: it has therefore been employed in the consideration of solvent effects on acids and bases, of neutralization and lyolysis (solvolysis), especially in non-aqueous media, and of certain aspects of amphoteric electrolytes. The changes mentioned have resulted in an increase of at least one-fifth in the size of the book, and in order to keep the volume within reasonable proportions the treatment of electrolytic oxidation and reduction has been restricted to fundamental principles, for the writer has recently published a comprehensive survey of the subject. As in the first edition, full references are given at every stage, but considerations of space have necessitated, in some instances, the omission of detailed mention of individual papers in favour of review articles containing complete bibliographies. In conclusion, thanks are due to Dr. A. Hickling for assistance in correcting the proofs, and to the author's wife for help in the preparation of the indexes and in many other ways.

S. G.

Feb. 1937

EXTRACT FROM PREFACE TO FIRST EDITION

FOR some time chemists have felt the need for a book of theoretical electrochemistry, especially in view of the recent important developments in connection with strong electrolytes and irreversible electrode phenomena. The present work has been written with the object of filling this gap in our scientific literature. Only an elementary knowledge of mathematics has been assumed, and an understanding of the first principles in physical chemistry should enable the student to follow all the arguments presented.

Several branches of electrochemistry still provide subjects for controversy, and wherever possible the author has attempted to give a critical survey of the present position; such surveys are bound to be influenced by the personal views of the writer, but it is probably better for a student to have a critical report rather than to find himself, without guidance, faced with a set of confusing data. In order, however, that the reader may obtain further details concerning both theoretical and practical aspects of the subjects discussed, a number of references to the original literature are given. Generally speaking, in addition to references to recent work, papers of historical interest and those containing reviews or literature summaries are mentioned.

The book has been restricted to the study of solutions, with special reference to aqueous solutions since they are more familiar and are understood better than non-aqueous solutions. Throughout the book, however, the latter are borne in mind and frequent reference to them is made, for it is realized that a study of these solutions is destined to play an important part in the future of electrochemistry.

The author would like to take this opportunity to express his thanks to Professor A. J. Allmand, F.R.S., for first arousing his interest in electrochemistry and for the help and encouragement which stimulated that interest. In writing this book the author has been influenced, to some extent, by all the books on electrochemistry he has ever read, and to all these he must express his indebtedness; particular mention should, however, be made of Foerster's *Elektrochemie wässriger Lösungen*, and of the article by Partington in Taylor's *A Treatise on Physical Chemistry*.

S. G.

Aug. 1930

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CHAPTER I

THE MECHANISM OF ELECTROLYSIS

ELECTRICITY is a form of energy, and when it passes through matter it may be converted into other forms, e.g. heat or chemical energy. The study of **electrochemistry** is concerned to a great extent with the interconversion of electrical and chemical forms of energy.

When plates of two dissimilar metals, e.g. zinc and copper, are placed in dilute sulphuric acid, the resulting system is a source of electricity called a **voltaic** or **galvanic cell**.^{*} If the plates are joined by a wire and a magnetic compass needle brought near to it, the needle will be deflected from its natural position; the wire also becomes warm. These effects, as well as others to which reference will be made later, are said to be caused by the passage, or flow, of a **current of electricity** through the wire. The direction in which the current is supposed to flow is defined in a purely arbitrary manner thus: if a man were swimming with the electric current and watching a compass needle, the north-seeking pole of the needle would turn towards his left side, and vice versa. By increasing the length of the wire connecting the plates of the voltaic cell the effect on the magnetic needle is decreased; hence the increased length of wire opposes the passage of the electric current. The property of hindering the flow of electricity is called **resistance**, and the long wire has a greater electrical resistance than the short.

Ohm's Law—The voltaic cell exerts an electrical pressure, or **electromotive force** (written *E.M.F.*), which is considered to drive the electric current through the wire. If two cells are connected together so that the copper plate of one is attached to the zinc plate of the other, and the remaining plates joined by a wire, the magnetic effect in the vicinity of the latter is twice that produced by a single cell. The two cells exert double the *E.M.F.* of each separate cell, and the magnitude of the current flowing is proportional to this force. The current strength thus depends on the *E.M.F.* of the cell and on the resistance of the circuit; the relation

^{*} Volta first discovered this method of producing an electric current; Galvani made some of the earliest experiments on electricity.

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between these quantities is given by Ohm's Law, which states that the current strength (I) varies directly as the *E.M.F.* (E) and inversely as the resistance (R), i.e.

$$I = E/R.$$

So far the deflection of a magnetic needle has been used to indicate the current strength, but a more accurate method is available. If the wire connecting the plates of the voltaic cell is severed and each end attached to a piece of platinum foil immersed in a solution of copper sulphate, metallic copper is deposited on the foil attached to the zinc plate of the cell. Similarly, silver is deposited if the copper sulphate is replaced by silver nitrate solution. It will be seen later that the weight of metal deposited in a given time is proportional to the strength of the current, and the unit of current is generally defined in terms of the weight of silver or copper it deposits in a given time. This unit is called the **ampere**, in honour of A. M. Ampère, one of the earliest investigators of current strength. The International ampere is defined as the current which flowing for one second will cause the deposition of 1.11800 milligrams of silver, or 0.3294 mgm. of copper, from solutions of their respective salts. The unit of electrical resistance is called an **ohm**, and the International ohm is the resistance at 0° C. of a column of mercury, of uniform cross-section, 106.3 cms. long and weighing 14.4521 gms. The volt is the unit of *E.M.F.*, the International value being defined as the difference of electrical potential required to maintain a current of one ampere through a system having a resistance of one ohm. It is thus possible to write Ohm's Law in the form :

$$\text{amperes} = \text{volts/ohms}.*$$

Quantity of Electricity—The weight of metal deposited by a current of electricity depends on its strength and on the time of flow; the product of these amounts (strength \times time) is called the 'quantity of electricity', the unit being the **coulomb**. This is

* The absolute ampere was originally defined as one-tenth of the current which flowing through a wire in the form of an arc 1 cm. long and of 1 cm. radius exerts a force of 1 dyne on a unit magnet pole placed at the centre of the arc; the more practical International ampere defined above has been found to be equal to 0.9993 absolute units. One absolute volt is 10^8 times the potential difference existing between two points when one erg of work must be expended to bring a unit of positive electricity from one point to the other; the International volt is 1.00045 absolute units. The International ohm on this basis must be 1.00052 absolute ohms. The International volt is sometimes defined in terms of the Weston cell, the *E.M.F.* of which is taken as 1.018300 I. volts at 20° (see p. 286); this makes the I. volt equal to 1.00042 absolute units. For practical purposes the International units are used, although the prefix is dropped.

defined as the quantity of electricity passing when 1 ampere flows for one second; hence each coulomb deposits 1.11800 mgms. of silver, or 0.3294 mgm. of copper. An apparatus in which the weight of metal deposited by the current can be determined may thus be used to measure the number of coulombs of electricity flowing through a conductor; such an apparatus is called a coulometer (p. 9).

Electrical Energy—When an electric current passes through a wire the electrical energy is converted into heat energy, and the amount of the latter may be measured in a calorimeter. It has been found that the heat generated is proportional to the quantity of electricity flowing, and to the *E.M.F.* driving it through the conductor. The unit of electrical energy is therefore defined as the energy developed when one coulomb is forced through a circuit by an *E.M.F.* of one volt; it is called the **volt-coulomb**, or **joule**. The magnitude of the volt and ampere were originally chosen in such a way that the volt-coulomb was exactly equal to 10^7 ergs, i.e. to 1 joule. This is not strictly true if International volts and amperes are used (see footnote, page 4); the International volt-coulomb, or International joule, is equal to 1.00032×10^7 ergs. From experiments on the mechanical equivalent of heat it has been found that 1 calorie is equivalent to 4.185×10^7 ergs, i.e. 4.185 absolute joules, and hence to 4.184 International joules or volt-coulombs. It follows, therefore, that 1 International volt-coulomb is equivalent to 0.2390 calories.*

Classification of Conductors—Although all forms of matter appear to be able to conduct the electric current, the conducting power, or **conductivity**, may vary over a wide range. Thus the conducting power of silver is more than 10^{24} times as great as that of a similar piece of paraffin-wax. It is not easy to draw a sharp line between good and bad conductors of electricity, but a rough division is possible; in electrochemistry the former type is generally encountered. In general, conductors may be grouped into three classes: (a) gaseous, (b) metallic and (c) electrolytic. Gases conduct electricity only with difficulty under the influence of high *E.M.F.*'s, or if exposed to the action of certain radiations; various phenomena are observed during the passage of electricity, but these will not be discussed here.

Metals are generally the best conductors of electricity. The passage of current through a metallic conductor causes no transfer of matter; hence the electricity is considered to be carried by the electrons, the atomic nuclei remaining stationary. This type of conduction is often called 'electronic conduction' and it is not

* The equivalence of heat and electrical and mechanical energy is based on the law of conservation of energy.

restricted to pure metals. Most alloys, carbon, and certain solid salts and oxides are the chief examples of electronic conductors. Electrolytic conductors, or **electrolytes**, are distinguished by the fact that when electricity passes through them there is an actual transfer of matter, which becomes apparent at certain points of discontinuity in the electrolyte. Electrolytic conductors are of two main types; the first consists of substances which conduct in the pure state, e.g. fused salts, fused metal hydrides, silver, barium, lead and other halides, and the α -form of silver sulphide.* Water, alcohols and other solvents are very poor conductors, but they may be placed in this class. The second group of electrolytic conductors is the one with which this book is mainly concerned; these conductors consist of solutions of one or more substances, e.g. a salt and water. The solvent need not necessarily be water; almost any liquid may be used, but the conducting power varies greatly with its nature. In addition to salts, acids and bases form electrolytic conductors in solution. Although these are the main solutes giving conducting solutions in water, other types of compound are effective in non-aqueous solutions; thus, lithium carbide dissolved in lithium hydride, and the alkaline earth nitrides dissolved in the corresponding fused hydride, are electrolytic conductors.† Solutions of organic acid amides and of nitro-compounds in liquid ammonia and in hydrazine conduct current electrolytically.‡ Aqueous electrolytes, in which the solvent is water, have been mainly studied and these will be considered in most detail.

'Mixed' Conductors—The line between electronic and electrolytic conductors is not sharp; it is probable that in the mixed oxides used for the filament of the Nernst lamp part of the current is carried electrolytically and part electronically. Solutions of the alkali and alkaline-earth metals are apparently mixed conductors in liquid ammonia,§ and so also is the β -form of silver sulphide, which conducts 80 per cent. of the current electrolytically.|| Further, some substances conduct electronically at one temperature and electrolytically at another; thus cuprous bromide changes its method of conduction between 200° and 330°.** Even in some liquid alloys, consisting only of metals which always conduct electronically, conduction involves a transfer of matter and appears to be related to

* Tubandt *et al.*, *Z. anorg. Chem.*, 1921, 115, 105; 117, 1; 1931, 197, 225; Schmidt, *Z. Elektrochem.*, 1924, 30, 440; Friedrich and Meyer, *ibid.*, 1926, 32, 566; von Hevesy, *ibid.*, 1932, 38, 504.

† Guntz and Benoit, *Compt. rend.*, 1923, 176, 970.

‡ Kraus and Bray, *J. Amer. Chem. Soc.*, 1913, 35, 1315; Garner *et al.*, *J. Chem. Soc.*, 1925, 127, 1227; Walden, *Z. physikal. Chem.*, 1934, 168, 419.

§ Kraus, *J. Amer. Chem. Soc.*, 1908, 30, 1323; 1914, 36, 864.

|| Tubandt, *loc. cit.*, 1921.

** Frers and Leopold, *Ber.*, 1928, 61, 377.

the electrolytic type. The passage of an electric current through sodium and potassium amalgams results in the transfer of appreciable amounts of alkali metal in a direction opposite to that of the flow of current ; * similar observations have been made on a number of molten alloys.†

Transport of Matter by the Electric Current—It has been stated that when an electric current is passed through an electrolytic conductor the transport of matter is only manifest at a discontinuity in the conducting system ; an example has already been given in connection with the deposition of copper from a copper sulphate solution (p. 4). The metal is deposited on the platinum foil connected to the wire attached to the zinc plate of the voltaic cell. In all current-producing cells there are two plates ; one of these is generally dissolved when current is produced and by convention it is called the negative pole of the cell ; the other plate usually has hydrogen or a metal deposited upon it and is called the positive pole. The current then always flows, outside the cell through the connecting system or circuit, from the positive to the negative pole. For example, in the simple zinc-copper cell, the zinc dissolves and hydrogen is liberated on the copper plate when current is drawn from the cell ; the zinc is, therefore, the negative pole and the copper is positive. Current is said to flow from the copper to the zinc outside the cell. In the Daniell cell, consisting of a zinc plate in zinc sulphate solution, separated by a porous partition from a copper plate in copper sulphate solution, the zinc dissolves and is the negative pole, whereas the copper is positive.

If the wire joining two poles of a cell is broken and the current allowed to pass through an electrolytic solution, e.g. a solution of silver nitrate, the plates which lead the current into and out of the electrolyte are called electrodes ; the one at which current enters, i.e. connected to the positive pole of the voltaic cell, is the positive electrode or **anode**, and the other, at which current leaves, the negative electrode or **cathode**. When an electric current passes through a solution of silver nitrate, or, as more usually expressed, during the electrolysis of the solution, silver is deposited on the cathode ; similarly other metals may be deposited on the cathode from solutions of their salts, and hydrogen may be liberated from acids. In general, if the anode is of gold or platinum, oxygen or halogen is evolved there, otherwise the metal will dissolve.

Faraday's Laws of Electrolysis—The relationship between the quantity of electricity passing through a solution and the amount of metal, or other substance, liberated at the electrodes was dis-

* Lewis *et al.*, *J. Amer. Chem. Soc.*, 1915, **37**, 2656.

† Kremann *et al.*, *Monatsh.*, 1924, **44**, 383, 401 ; 1924, **45**, 133, 157, 177, 311, 339, 379, 385 ; 1930, **56**, 35 ; *Z. physikal. Chem.*, 1924, **110**, 559.

covered by Faraday* as the consequence of a long series of researches. He expressed the results of his work in two quantitative laws, which may be stated as follows:

I. The amount of chemical decomposition produced by a current, or the amount of any substance deposited, is proportional to the quantity of electricity passing through the electrolyte.

II. The amounts of different substances deposited, or liberated, by the same quantity of electricity are proportional to their chemical equivalent weights.

Faraday's laws may be tested by passing a current simultaneously through a number of different solutions, e.g. dilute sulphuric acid, silver nitrate and copper sulphate; if a current of one ampere

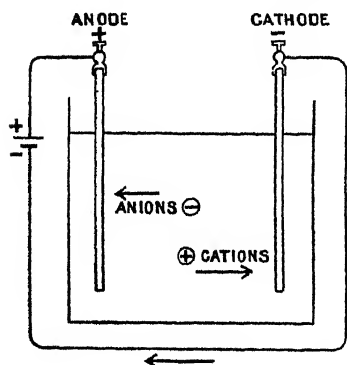


FIG. 1.—Illustration of terms used in electrochemistry

flows for one hour the weights liberated are 0.6266 mgm. of hydrogen, 67.08 mgms. of silver and 19.91 mgms. of copper. These quantities are in the ratio of 1 to 107.88 to 31.78, which is the ratio of the equivalent weights. Should a current of two amperes flow for one hour the amounts deposited are doubled.

The Faraday—By definition one coulomb of electricity sets free 0.001118 gram of silver from a solution of a silver salt; the equivalent weight of silver is 107.88 and so $107.88/0.001118$, i.e.

96,494 coulombs should be required to liberate 1 gm. equivalent of silver, and consequently of any other element. The value generally used at present is 96,500 coulombs,† and this is called a faraday (*F*); the passage of 1 faraday liberates 1 gm. equivalent of any substance. During the electrolysis of certain solutions two substances are sometimes liberated at the cathode; for example, in the electrolysis of nickel sulphate solution both nickel and hydrogen may be set free. One faraday of electricity causes the separation

* *Phil. Trans.*, 1833, 123, 23; 1834, 124, 77.

† This is strictly true for absolute coulombs only. According to the International Critical Tables, one faraday is equal to 96,510 International coulombs, on the basis of the defined *E.M.F.* of the Weston cell, and 96,507 based on the definition of the ampere. The discrepancy between 96,494 and 96,507 is attributed to the fact that 0.001118 gm. is supposed to represent the gross deposit of silver, which may include impurities (see Clark, *The Determination of Hydrogen Ions*, 1928, p. 248). The situation is, however, unsatisfactory and it seems best to adopt a value of 96,500 for the present.

of a *total* of one equivalent, part of which is nickel and part hydrogen. Since 96,500 amperes (abbreviated as 'amps.') flowing for one second liberate e grams of any substance, where e is the equivalent weight, then I amps. flowing for t seconds will cause the deposition of $Iet/96,500$ gms.; this formula is the mathematical expression of Faraday's laws.

The accuracy of the laws has been subjected to very rigorous test under a variety of conditions; Richards and Stull* found that a given quantity of electricity deposited the same weight of silver from a solution of silver nitrate in water at 20° or in fused sodium and potassium nitrates at 250°. Faraday's laws hold for various solvents other than water,† for solid electrolytic conductors,‡ and for fused electrolytes.§ There are one or two apparent exceptions to Faraday's laws, but they are readily explained. The amount of sodium liberated at the anode in the electrolysis of a solution of the metal in liquid ammonia is less than would be expected; this is because only part of the current is carried electrolytically and part electronically. When due allowance is made for this it is found that Faraday's laws are obeyed. Smyth|| observed that when a solution of sodium in liquid ammonia is saturated with lead and electrolysed, 2.26 gm. atoms of lead are deposited on the anode for every faraday of electricity passing; similar abnormalities were observed in the electrolysis of sodium-antimony solutions in liquid ammonia.** In each case the substances present are not those found in aqueous solutions; the lead and antimony, respectively, exist in the form of complexes.

Measurement of Quantity of Electricity—Since the weight of any substance liberated at an electrode is given accurately by the expression $Iet/96,500$ gms., the method of weighing the electrolytic deposit may be utilized in the exact measurement of quantity of electricity, or of current strength. An apparatus by means of which this may be done is called a voltameter, or better, a coulometer.††

The Silver Coulometer is probably the most accurate; it has been carefully examined by many investigators and the conditions for obtaining accurate results have been described by Rosa

* *Z. physikal. Chem.*, 1903, **42**, 621.

† Kahlenberg, *J. Physical Chem.*, 1900, **4**, 349; Speransky and Goldberg, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 797; Steele, McIntosh and Archibald, *Phil. Trans.*, 1906, **206 A**, 122.

‡ Tubandt and Lorenz, *Z. physikal. Chem.*, 1914, **87**, 513; Tubandt and Eggert, *Z. anorg. Chem.*, 1920, **110**, 196.

§ Helfenstein, *ibid.*, 1900, **23**, 255; Richards and Stull, *loc. cit.*

|| *J. Amer. Chem. Soc.*, 1917, **39**, 1299.

** Peck, *ibid.*, 1918, **40**, 335.

†† Richards and Heimrod, *Z. physikal. Chem.*, 1902, **41**, 302 footnote.

and Vinal* as follows. The electrolytic cell should contain 10–20 gms. of silver nitrate in 100 c.c. of solution, and be free from organic matter, or other reducing substances, and colloids. The silver nitrate must be very pure, crystallized from acid solution and fused, repeatedly if necessary. The coulometer should contain not less than 75 c.c. in the cathode compartment and the concentration at the surface of the cathode should not be reduced during electrolysis below 5 per cent. The electrolyte must be neutral, or very slightly acid, before and after electrolysis. The anode should be of pure silver, preferably coated with silver by electrolysis; the cathode may be a platinum basin. The liquids in the two compartments should be separated either by a glass cylinder fitting round the anode† or by a porous pot.‡ The cathode basin is washed at the end of the electrolysis, dried at 150° and weighed; from the gain in weight the number of coulombs passing can be calculated. Since nitrate solutions do not always give smooth deposits of silver, an electrolyte made by dissolving silver oxide in a solution of hydrofluoric and boric acids has been proposed for use in a coulometer. It is said to give accurate results and the deposits are smooth.§ A simple form of silver coulometer for less accurate work has been designed in which the silver dissolved at the anode (see p. 12) is determined volumetrically.||

The Iodine Coulometer has been found to give a reproducibility within 0.002 per cent. for the iodine liberated at the anode from a solution of potassium iodide.** The quantity of iodine produced can be determined by titration, and the results are in very close agreement with those calculated from measurements with the silver coulometer. These results provide an accurate verification of Faraday's laws.

The Electrolytic Gas Coulometer—This type of coulometer is only of use for the rough measurement of very small quantities of electricity. The electrolyte may be dilute sulphuric acid or a solution of sodium, potassium or barium hydroxide; the electrodes are of platinum for acid solutions, but nickel may be used in alkaline electrolytes.†† In either case hydrogen and oxygen are liberated and the mixed gases may be collected; the total volume is measured at a known temperature and pressure. One faraday liberates 1 gm. of hydrogen and 8 gms. of oxygen, occupying a total volume of 16.8 litres at N.T.P.

* *Bureau of Standards, U.S.A., Scientific Paper*, No. 285, 1916.

† Smith (F. E.), *National Physical Laboratory Report*, 1910, p. 32.

‡ Richards, *Z. physikal. Chem.*, 1900, 32, 336.

§ von Wartenberg and Schütza, *Z. Elektrochem.*, 1930, 34, 254.

|| Kistiakowsky, *ibid.*, 1906, 12, 713.

** Washburn and Bates, *J. Amer. Chem. Soc.*, 1912, 34, 134.

†† Cf. Riesenfeld, *Z. Elektrochem.*, 1906, 12, 621.

The Copper Coulometer—For most occasions, in the laboratory and in industry where great accuracy is not required, the copper coulometer is used; in this apparatus the weight of copper deposited from a copper sulphate solution is determined.* It is recommended that two parallel sheets of copper be used as anodes, and a thin sheet of copper be placed midway between them to act as cathode. One litre of the electrolyte should contain 125–150 gms. of crystallized copper sulphate, 50 gms. pure sulphuric acid and 50 c.c. of ethyl alcohol; the object of the latter is to prevent dissolution of the deposited copper by oxidation, and tartaric acid may be used instead. The strength of the current should be between 0.002 and 0.02 amp. per sq. cm. of cathode surface; during electrolysis the solution should be gently stirred by a stream of carbon dioxide.† At the end of the deposition the cathode is removed, washed with water and dried in an air oven at 100°. One coulomb deposits 0.0003294 gm. of copper.

The Mercury Coulometer—This instrument is used for the measurement of large quantities of electricity, e.g. for lighting, heating or power, in the Wright Electrolytic Meter.‡ The electrolyte is a solution of mercuric iodide in potassium iodide solution, and the quantity of mercury liberated is determined by measuring its volume in a standardized tube. From the indications of the mercury level the number of coulombs which have passed may be read off directly with an accuracy of 1 per cent. A form of mercury coulometer has also been used by Lehfeldt§ to measure minute currents of long duration.

The Sodium Coulometer—This coulometer is of an unusual type and is mainly of interest in showing that Faraday's laws apply in somewhat exceptional circumstances; it is said to be capable of yielding results accurate to 0.01 per cent., although a relatively high voltage is required. The electrolyte consists of fused sodium nitrate at 340° and the electrodes are soft glass tubes, electrical contact being made by means of molten cadmium in the cathode, and cadmium containing a little sodium in the anode. When a current is passed elementary sodium is deposited in the glass of the cathode and migrates out of the anode; the quantity of electricity flowing is determined by the gain or loss in weight, respectively. Owing to the possibility of loss of silicate ions from the

* Oettel, *Chem.-Ztg.*, 1893, 17, 543, 577; Datta and Dhar, *J. Amer. Chem. Soc.*, 1916, 38, 1156.

† For modifications of the Copper Coulometer, see Marshall, *Trans. Faraday Soc.*, 1925, 21, 297; Matthews and Wark, *J. Physical Chem.*, 1931, 35, 2345.

‡ Hatfield, *Z. Elektrochem.*, 1909, 15, 728; for full description see Allmand and Ellingham, *Applied Electrochemistry*, 1924, p. 20.

§ *Phil. Mag.*, 1902, 3, 158.

cathode it is said that more accurate results are obtained with the anode.*

Anodic Dissolution—If the anode is of platinum or other unattackable material, oxygen, or chlorine, may be liberated in amounts required by Faraday's laws, after allowing for the quantities remaining dissolved in the electrolyte. Attackable metals, e.g. zinc, copper, iron, mercury, generally dissolve when used as anodes, and oxygen evolution does not occur. The weight of metal dissolved is equal to the amount that would be deposited at the cathode in accordance with Faraday's laws. Thus 1 coulomb causes 1.118 mgms. of silver, or its equivalent, to dissolve. Some metals are able to form two differently charged ions, e.g. mercury, copper, and the passage of 1 faraday (96,500 coulombs) results in the dissolution of a *total* of 1 gm. equiv. of the metal, allowing for the amounts in the different valency conditions. In some cases, e.g. passive nickel in a chloride solution (see Chap. XIX), the metal dissolves and oxygen is evolved simultaneously; the *sum* of the number of equivalents of nickel dissolved and of oxygen liberated is in agreement with Faraday's laws.

The Phenomena and Mechanism of Electrolysis—In the year 1800 Nicholson and Carlisle† observed that when a current of electricity was passed through water oxygen was liberated at one electrode and hydrogen at the other; at the same time it was found that the water became alkaline around the electrode from which the hydrogen was liberated, and acid near the other. A year or two later Davy showed that if an electric current is passed through 'pure' water no acidity or alkalinity results; it was suggested that the formation of acid and alkali in the experiments of previous investigators was due to impurities in the water. The work of Berzelius and Hisinger‡ established the fact that in the electrolysis of solutions of alkali metal salts, e.g. potassium sulphate and sodium chloride, alkali was produced at one electrode and acid at the other; these results, and others, led Berzelius§ to propose his electro-chemical or dualistic theory of combination. According to this theory a salt, e.g. potassium sulphate, resulted from the combination of a positively charged alkaline oxide (K_2O)⁺, and a negatively charged acidic oxide (SO_3)⁻; || the effect of the electric current was to draw the acid and base towards the electrodes by the

* Burt, *Physical Rev.*, 1926, 27, 813; Stewart (O. J.), *J. Amer. Chem. Soc.*, 1931, 53, 3366.

† *Nicholson's Journal*, 1800, 4, 179.

‡ *Ann. de Chim.*, 1804, 51, 172; *Gilb. Annalen*, 1807, 27, 270.

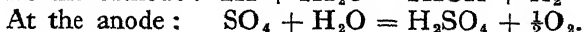
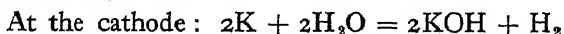
§ For review of the work of Berzelius, see Duschultz, *Z. Elektrochem.*, 1930, 36, 57.

|| The formula of potassium sulphate at the time of Berzelius was accepted to be KSO_4 .

attraction of opposite charges. The theory of Berzelius held the chemical field until further work by Daniell and others* showed it to be untenable. Daniell passed a given current of electricity through a dilute solution of sulphuric acid and one of potassium sulphate; the same quantities of hydrogen and oxygen were liberated at the electrodes in each case, but in the latter solution acid and alkali were formed in amounts equivalent to the gases liberated. According to the theory of Berzelius the hydrogen and oxygen result from the decomposition of the water, but the acid and alkali are produced from the salt; hence half as much current should be required to produce the gases alone, as would be required for the gases in addition to equivalent amounts of acid and alkali. Daniell's experiment showed that this was not the case, and if Faraday's laws of electrolysis were to be accepted the Berzelius theory was untenable.

Ions—In order to account for some of the phenomena observed during the passage of an electric current through a solution, Faraday assumed that the flow of electricity was associated with the movements of particles of matter carrying either positive or negative charges of electricity; these particles he called **ions**.† The ions carrying a positive charge and moving in the direction of the electric current, i.e. towards the cathode, he called **cations**, and those carrying a negative charge and moving in the opposite direction, i.e. towards the anode, were called **anions** (see Fig. 1).‡ On reaching the electrode the ion was assumed to give up its charge, or have it neutralized, and be deposited as an ordinary atom. Thus a positively charged silver ion travels towards the negative electrode, or cathode, under the influence of the electric field; there its charge is neutralized and it is deposited as ordinary silver.

In attempting to explain his observations on the electrolysis of potassium sulphate solution Daniell made use of Faraday's concept of ions. The ions present were assumed to be K^+ and SO_4^{--} , which travel towards the cathode and anode, respectively. On reaching the electrodes they become discharged and liberate K and SO_4 ; but neither of these is stable in water, and so the following secondary reactions § ensue:



It follows, therefore, that the amount of alkali set free at the cathode must be equivalent to the acid liberated at the anode, and both are equivalent to the hydrogen and oxygen evolved. Further, the re-

* *Phil. Trans.*, 1839, 129, 97; 1840, 130, 209; 1844, 134, 1.

† From the Greek word meaning 'wanderer'.

‡ These terms are still used in modern electrochemistry.

§ Modern formulæ and symbols are used.

sults are in agreement with Faraday's laws, since the acid, alkali, oxygen and hydrogen are assumed to be secondary products of electrolysis. The primary products K and SO_4 are certainly discharged in amounts corresponding with the requirements of the laws. This theory was accepted for many years to explain the phenomena of the electrolysis of alkali metal salts, and is still quoted in some text-books; there is, however, another view which is preferable in many ways (see p. 414).

The Charge on an Ion—The conception of valency introduced by Frankland in 1852 has thrown light on the question of the number of charges carried by an ion. Since 1 faraday liberates 1 gm. equiv. of any ion, it may be assumed that each equivalent carries the same unit charge, namely 96,500 coulombs. The gram-ion is equal to the gm. equiv. multiplied by the valency of the atom or group forming the ion; hence the number of unit charges on an ion is equal to its valency. If n is the valency of the atom or group of atoms, and F represents 1 faraday (96,500 coulombs), the total charge carried by the gram-ion is nF coulombs.

The Mechanism of Electrolytic Conduction *—The first definite idea of the processes occurring in an electrolyte during the passage of an electric current was suggested by Grotthuss; † he maintained that the action of the electric field is to orient the molecules of electrolyte in chains, so that the negative parts (according to Berzelius) point towards the positive electrode and vice versa. The electrodes then attract the ends of the chain; the positive part of one end molecule is thus liberated at the negative electrode, and the negative part of the other end molecule separates at the positive electrode. The residual parts of the end molecules are then supposed to exchange 'partners' with adjacent molecules, and this interchange is carried on until a complete series of new molecules is formed. These are again oriented by the current, split up and so on. Objection has been made to this theory mainly on the ground that only very small *E.M.F.*'s are required in many electrolytic processes, whereas the views of Grotthuss imply the necessity of a large force sufficient to break a molecule into its component parts. The theory in any case does not give a picture of electrolytic conduction, but only of the processes resulting in the deposition of substances at the electrodes.

Origin of the Ions—Although Faraday realized the existence of charged particles, or ions, in solution he did not speculate in any way on their number or origin. In 1857, however, Clausius ‡

* See Mellor, *Comprehensive Treatise of Inorganic Chemistry*, Vol. I, 1922, p. 969; Taylor, *Physical Chemistry*, 1931, p. 629 (Partington).

† *Ann. Chim. Phys.*, 1806, 58, 54; 1808, 63, 20.

‡ *Ann. Physik*, 1857, 101, 338.

suggested that the positive and negative parts of a molecule were not firmly connected, but were each in a state of vibration which often became vigorous enough to cause the portions to separate. The separated parts soon become attached to particles of opposite sign, originating possibly from other molecules, and so only remained free momentarily; these charged particles, or ions, during their short periods of free existence, were supposed to carry the current. According to Clausius only a small fraction of the total number of dissolved molecules was split up into ions; and as these ions were discharged at the electrode, or removed by other means, they were continually replaced by fresh ions resulting from vibration or from collisions between molecules. On the basis of this mechanism of electrolysis only very small *E.M.F.*'s are required to guide the ions to the electrodes; no electrical energy is apparently used up in dividing the molecule. This concept was found satisfactory until 1887, when Arrhenius published his theory of 'electrolytic dissociation', which forms the basis of modern views on electrolysis.

The Electrolytic Dissociation Theory *—In a paper read before the Swedish Academy of Sciences in 1885, van 't Hoff † showed both theoretically and experimentally that the gas laws are approximately applicable to dilute solutions. Consequently if 1 gm. mol. of a solute is dissolved in a volume V of solvent, the osmotic pressure P of the resulting solution at the absolute temperature T should be given by the expression

$$PV = RT,$$

where R is the gas constant, equal to 8.315×10^7 ergs.

Although this generalization held for many solutions, mainly involving organic solutes, it was not true for aqueous solutions of acids, bases and salts, i.e. for electrolytes. In such cases the value of the osmotic pressure is two or three times as great as that expected from the gas law equation. Similar abnormalities occur in the freezing-point depression and in the elevation of boiling point, both of which are proportional to the osmotic pressure of the solution. To overcome this difficulty van 't Hoff suggested the inclusion in the equation of an empirical factor i ; this was first regarded as a constant, but was later shown to vary with the concentration. The gas laws for the abnormal solutions were then expressed in the form

$$PV = iRT$$

for 1 gm. mol. of solute. The value of i is, therefore, given by :

* See *Alembic Club Reprints*, No. 19, for the most important classical papers.

† *Z. physikal. Chem.*, 1887, 1, 481; *Phil. Mag.*, 1888, 26, 81.

$$\begin{aligned}
 i &= \frac{\text{Actual Osmotic Pressure}}{\text{Theoretical Osmotic Pressure}} \\
 &= \frac{\text{Actual Elevation of Boiling Point}}{\text{Normal Elevation of Boiling Point}} \\
 &= \frac{\text{Actual Depression of Freezing Point}}{\text{Normal Depression of Freezing Point}}
 \end{aligned}$$

The normal values of the elevation of boiling point may be determined experimentally by using a non-electrolyte of known molecular weight, e.g. cane sugar or urea; they may also be calculated from latent heats by the use of thermodynamic equations deduced by van 't Hoff.

The Arrhenius Theory—In the year 1883 Arrhenius * published the results of investigations on the electrical conductivity of solutions, from which he concluded that an electrolyte contained two kinds of solute molecules; these were supposed to be 'active' molecules, responsible for electrical conduction, and inactive molecules. Further, it was suggested that in very dilute solutions all the inactive molecules were converted into active. The assumption was made that when an acid, base or salt was dissolved in water a *considerable portion*, the so-called active molecules, became 'dissociated' into positively and negatively charged particles, or ions. These ions are free to move independently, and they are simply guided towards the electrode of opposite sign under the influence of the electric field. The proportion of 'active', or 'dissociated', molecules to the total number of molecules, i.e. the 'degree of dissociation', was believed to vary with the concentration of the electrolyte, and to be equal to unity in dilute solutions. This, in outline, was the theory of **electrolytic dissociation**, or ionization, as proposed by Arrhenius.

When the work of van 't Hoff, referred to in the previous section, was published, Arrhenius saw the significance of the results for his own theory, and he used them in a manner which lent it strong support.† Suppose each molecule when it dissociates yields ν ions, then if a solution contains a total of m molecules in a given volume, and α is the fraction of these molecules that are dissociated, there will be present $m(1 - \alpha)$ undissociated molecules, and $\nu m\alpha$ ions, i.e. a total of $m - m\alpha + \nu m\alpha$ particles. The osmotic pressure, like the gas pressure, may be taken as proportional to the number of individual molecular particles in a given volume; therefore the van 't Hoff factor may be written as equal to :

* *Bihang der Stockholmer Akad.*, 1883, 8, Nos. 13 and 14.

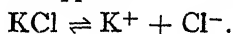
† *Z. physikal. Chem.*, 1887, 1, 631.

number of particles actually present

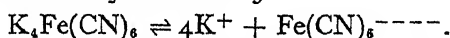
 number of particles which would have been present had there been no dissociation

$$\text{that is } i = \frac{m - m\alpha + m\nu\alpha}{m} = 1 - \alpha + \nu\alpha.$$

For potassium chloride, and other simple binary salts, ν is equal to 2, since dissociation is supposed to occur thus :



As a general rule the metallic part of a salt, or hydrogen in an acid, constitutes the positive ion (cation) ; the acidic portion forms the negative ion (anion). With barium chloride, ν is equal to 3, and for potassium ferrocyanide it is 5 :



It appears, therefore, that the van 't Hoff factor i may be calculated either from freezing-point measurements, or from a knowledge of the degree of dissociation of an electrolyte ; Arrhenius suggested a method for calculating the latter from conductance* measurements, and hence was able to calculate i , on the basis of his theory, without reference to osmotic or allied effects. Some of the values, given by Arrhenius, for i determined by freezing-point and conductance methods are quoted in Table I. They refer to aqueous solutions containing 0.1 gm. mol. of solute in 1 litre of solvent.

TABLE I
 PARISON OF VAN 'T HOFF FACTOR OBTAINED FROM FREEZING-P.
 AND CONDUCTANCE DATA

Substance.	F.-Pt.		Cond.	
	i	α	i	α
Hydrochloric acid . . .	1.98	0.98	1.90	0.90
Nitric acid . . .	1.94	0.94	1.92	0.92
Sulphuric acid . . .	2.06	0.53	2.19	0.59
Oxalic acid . . .	1.25	0.12	1.49	0.24
Acetic acid . . .	1.03	0.03	1.01	0.01
Sodium hydroxide . . .	1.91	0.91	1.93	0.93
Potassium hydroxide . .	1.79	0.79	1.90	0.90
Barium hydroxide . . .	2.69	0.84	2.67	0.83
Sodium chloride . . .	1.90	0.90	1.82	0.82
Potassium chloride . . .	1.82	0.82	1.86	0.86
Ammonium chloride . . .	1.88	0.88	1.84	0.84
Sodium acetate . . .	1.73	0.73	1.79	0.79
Potassium sulphate . . .	2.11	0.55	2.33	0.66
Potassium oxalate . . .	2.43	0.71	2.32	0.66
Mercuric chloride . . .	1.11	0.05	1.05	0.02

The close parallelism between the values of i determined by the two quite distinct methods suggests that there is a strong probability in favour of the assumptions on which the calculations are

* The method will be discussed later, see p. 78.

based. These assumptions are (a) that the gas laws hold for *all* solutions, provided the correct number of molecular particles is considered; (b) that every electrolyte contains a proportion of molecules which have dissociated, or ionized;* and (c) that the proportion of dissociated to undissociated molecules may be determined from conductance measurements. According to these measurements the fraction of dissociated molecules (α) should increase with increasing dilution, and so also, therefore, should i with which it is related; the results† in Table II confirm this view, and lend general support to the dissociation theory.

TABLE II
VARIATION OF THE VAN 'T HOFF FACTOR WITH CONCENTRATION OF ELECTROLYTE

Sodium Chloride.				Sodium Sulphate.			
Gm.	Mols./Litre.	i		Gm.	Mols./Litre.	i	α
0.0467	. . .	2.00	1.00	0.028	. . .	2.66	0.83
0.117	. . .	1.93	0.96	0.0701	. . .	2.46	0.73
0.324	. . .	1.86	0.93	0.117	. . .	2.33	0.66
0.539	. . .	1.85	0.92	0.195	. . .	2.21	0.60

It will be clear from the historical outline given that the Ionic Theory did not originate with Arrhenius; Faraday, and others, realized that electrolytes must contain charged particles which carried the current and were discharged at the electrodes. Arrhenius co-ordinated the work of the earlier investigators, and suggested that the ions were spontaneously produced in large proportions when an electrolyte was dissolved in water. His clear statement of the theory of electrolytic dissociation marked the commencement of a new era in the study of electrolytes. On the whole it may be said that the research stimulated by the theory has helped to substantiate it, but it has brought to light certain defects which indicate that some modification is necessary. In the first place, it is now considered doubtful if the methods used by Arrhenius to calculate the degree of dissociation are justified. The agreement between the two sets of values given in Table I is probably to a great extent fortuitous; in any case, a closer examination has shown that the agreement is not so good as at first appeared. In spite of this, and other weaknesses to be discussed later, the main assumption, that an electrolyte ionizes or dissociates spontaneously when it is dissolved, is now almost universally accepted. For the present, therefore, the Arrhenius theory will be adopted as a basis for the study of electrolytes and electrolysis.

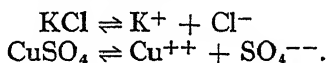
Classification of Electrolytes—An examination of Table I (p. 17) shows that the substances mentioned there may be divided

* The term 'active molecule', in this sense, is no longer used.

† Arrhenius, *Z. physikal. Chem.*, 1888, 2, 496.

roughly into two groups according to the value of α , the so-called degree of dissociation. The mineral, or strong, acids, the hydroxides of alkali and alkaline-earth metals (the strong bases), and most salts are considerably dissociated at the concentration of 0.1 *N*, for which the figures are given; these substances are called **strong electrolytes**. On the other hand, the weak inorganic acids, most organic acids and phenols, ammonia and most organic bases, and certain salts, e.g. mercuric chloride and cyanide, are classed as **weak electrolytes** since they are only slightly dissociated at normal concentrations. It should be noted that salts of weak acids, or of weak bases, are quite appreciably dissociated. It is impossible, however, to group all electrolytes into 'strong' and 'weak' types; although this forms a convenient rough division, there are many instances of intermediate cases (see p. 174).

Electrolytes are sometimes classified according to the number and valency of the ions produced; thus potassium chloride and copper sulphate would both be termed 'binary' electrolytes, since each molecule yields two ions, thus

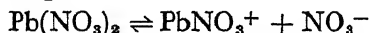


and

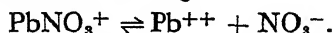
The former is, however, called a uni-univalent electrolyte, and the latter bi-bivalent; the valencies of the ions are given in the order positive-negative. Barium chloride and sodium sulphate are ternary electrolytes; but the former is bi-univalent, and the latter uni-bivalent. Binary electrolytes are generally assumed to ionize in one stage, but ternary electrolytes may dissociate in two stages:



The extent to which the second stage of dissociation has occurred at any particular concentration depends on the nature of the electrolyte; in a 0.1 *N*-solution of sulphuric acid it is very marked, but it is much less, if it has occurred at all, in oxalic and sulphurous acids. Ternary salts also ionize in stages; in a 0.1 *N*-lead nitrate solution the first stage

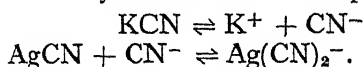


predominates over the second stage

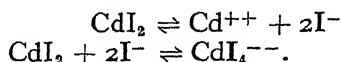


This is an interesting case because here the acidic portion of the salt (NO_3) is included in the positive ion, PbNO_3^+ , and is an example of 'complex-ion' formation. There are many instances of complex ions in which the metal forms part of the negative ion, or anion; such ions usually result from the combination of the simple anion with undissociated molecules of the salt. Silver cyanide

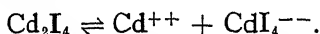
dissolves in excess of potassium cyanide to form a complex anion containing silver, $\text{Ag}(\text{CN})_2^-$; it is formed by the union of undissociated silver cyanide with cyanide ions from the potassium cyanide:



In some cases 'internal' complex-ion formation occurs; then some of the undissociated molecules unite with the ions produced by the dissociated ones. Cadmium iodide is an excellent example (see p. 40):



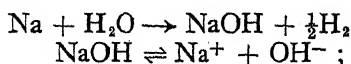
Alternatively it may be supposed that double molecules Cd_2I_4 are formed, and these ionize:



The subject of complex ions will be dealt with more fully at a later stage.

Objections to the Theory of Electrolytic Dissociation—

When the theory of Arrhenius was first published it met with opposition, mainly because it involved ideas which seemed revolutionary at the time, but are now accepted as commonplace. It appeared impossible to believe that an element like sodium, able to attack water vigorously, should exist in aqueous solution as an ion formed when sodium chloride dissolved quietly in water. Further, since sodium and chlorine atoms combine to form sodium chloride with a large evolution of heat, it could not be credited that the sodium chloride would disintegrate spontaneously into sodium and chlorine ions immediately it was dissolved in water. These difficulties were based on a failure to understand the distinction between an atom and an ion; the presence of an electric charge profoundly modifies the properties of an atom. According to modern theories of atomic structure it is on account of the strong tendency of the sodium atom to become an ion that it attacks water so vigorously, thus:



and

it is the ion which is the stable form of sodium, since it has its electronic groups complete without residuary electrons.* Similarly in the reaction between sodium and chlorine the energy is liberated, to a great extent, because of the conversion of the unstable atoms into the stable ions; these are probably present as such in the solid salt (p. 134).

The dissociation theory has been criticized on the grounds of

* See, for example, Sidgwick, *The Electronic Theory of Valency*.

the supposed impossibility of separating from one another the positive and negative ions. A partial separation of the ions was accomplished by Nernst and Ostwald,* but more definite results were obtained by Tolman,† who whirled solutions of various iodides by means of a powerful centrifugal machine; the ends of the tubes in which the solutions were placed acquired opposite charges. This separation of charge was probably due to the accumulation of the heavier (iodine) ions at one end, and the lighter, oppositely charged ions at the other; the result, therefore, is in harmony with the dissociation theory.

Instantaneous reactions in solution are generally ascribed to the interaction of ions, but it has been claimed by Kahlenberg and his co-workers ‡ that double-decomposition occurred instantaneously when dry hydrochloric acid gas was passed into solutions of the heavy metal salts of the higher organic acids in benzene; the solutions, however, had no conducting power before or after the experiment. These results were interpreted as being opposed to the dissociation theory, but whether this interpretation is correct, or not, is immaterial, since it has been shown § that the salt solutions used by Kahlenberg had a small but definite conductivity, and this increased on the passage of hydrochloric acid gas before the sodium chloride was precipitated. The conductance indicates the presence of a sufficient number of ions to account for the reactivity of the solution.

One of the chief opponents of the theory of electrolytic dissociation has been H. E. Armstrong;|| he suggested that the behaviour of electrolytes may be explained by assuming the presence in solution of active and inactive hydrated molecules of salt. The theory does not, however, appear to be capable of quantitative treatment, and 'involves many fresh assumptions for which there is no *a priori* reason'.** As a working hypothesis it certainly has no advantages over the dissociation theory, and the same may be said concerning the views of Snethlage,†† which have been criticized by Dhar.‡‡ Although the original theory of electrolytic dissociation must be modified, mainly as a result of work on strong electrolytes (see Chap. VII), there is no reason for its abandonment.

* *Z. physikal. Chem.*, 1889, 3, 120.

† *J. Amer. Chem. Soc.*, 1911, 33, 121.

‡ *J. Physical Chem.*, 1901, 5, 339; 1902, 6, 1; 1906, 10, 593; 1911, 15, 97.

§ Cady *et al.*, *J. Amer. Chem. Soc.*, 1913, 35, 1434; 1921, 43, 646.

|| *J. Chem. Soc.*, 1895, 67, 1122; *Nature*, 1896, 55, 78; *Proc. Roy. Soc.*, 1906, 78 A, 264; 1907, 79 A, 564; 1908, 81 A, 80; 1923, 103 A, 610; see also Kling and Lassieur, *Compt. rend.*, 1923, 177, 109, for similar views.

** Findlay, *Ann. Reports Chem. Soc.*, 1907, 4, 21.

†† *Z. physikal. Chem.*, 1915, 90, 1, 139.

‡‡ *Trans. Faraday Soc.*, 1919, 15, 81.

CHAPTER II

TRANSPORT NUMBERS AND IONIC MIGRATION

THE Migration of Ions—The quantity of electricity that can be carried by an electrolyte, i.e. its conductance, or conducting power, depends on (a) the number of ions present, (b) the charge carried by each ion, and (c) the velocity at which the ions move. The number of ions in the solution depends on its concentration and on the degree of dissociation; this matter will be discussed later. The charge carried by each ion, as has already been seen (p. 14), depends on its valency. In the present chapter the question of ionic velocity will be considered. Although the early workers in electrochemistry had probably realized that different ions moved with different speeds, experimental difficulties prevented a study of the subject. In 1853, however, Hittorf* showed that the velocities of the ions could be correlated with the concentration changes in the vicinity of the electrodes. The faster-moving ion will obviously cause a greater depletion of concentration in the electrode compartment from which it moves away than will the slower ion.

It is almost invariably found that in any electrolyte the two ions move with different speeds, yet equivalent quantities of each ion are liberated at the anode and cathode, as required by Faraday's laws. This fact may appear puzzling, but a little consideration will show that it must hold good. Electricity may be carried through an electrolyte in either one or both of two ways; positive charges may be carried in one direction by cations, or negative charges in the opposite direction by the anions. The total quantity of electricity passing through the solution is the sum of these two separate amounts; for every 96,500 coulombs of electricity, carried by positive and negative ions together, 1 gm. equiv. is liberated at each electrode. Consequently, even if one of the ions does not move *at all*, and so carries none of the current, electricity can still be carried by the other ion,† and equivalent amounts of anions and cations are discharged.

* *Ann. Physik*, 1853, 89, 177.

† In the case of certain solid and fused electrolytes it is quite common to find that all the current is carried by one kind of ion, and yet equivalent

Ionic Migration and Concentration Changes—A simple method of studying this subject is by means of the diagram * in Fig. 2, which represents a number of positive and negative ions distributed evenly between two electrodes *A* and *B*, anode and cathode respectively. The space between the electrodes is supposed to be divided into three sections by two partitions *C* and *D*, real or imaginary; section *AC* is called the anode compartment, *CD* the middle compartment, and *DB* the cathode compartment. At the commencement of electrolysis the ions are at equal concentrations in each section, and equal numbers of anions and cations are present (Fig. 2, I). Suppose that the cations *only* are able to move and that in a given time, under the influence of an applied *E.M.F.*,

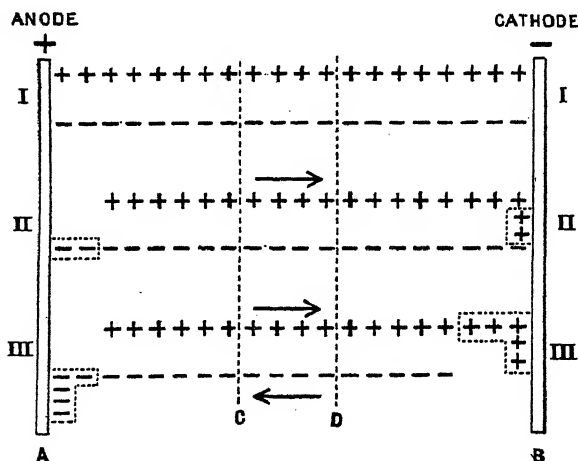


FIG. 2.—The migration of ions and concentration changes

two of these ions move across the partitions from left to right; two faradays of electricity will have passed through the solution, and the condition reached will be as in Fig. 2, II. At each electrode there are two ions un-paired and these are considered to be discharged; thus, although only positive ions can move, when two faradays of electricity pass through the cell two gm. equivs. are discharged at *each* electrode. It may be observed that the anode compartment, which originally contained eight, now only contains six of each kind of ion; that is, it has its concentration decreased by two gm. equivs. of electrolyte. The cathode compartment,

amounts of both ions are liberated at the electrodes; for references see the work of Tubandt *et al.*, mentioned in Chapter I (p. 6).

* For a rigid discussion of the significance of this type of diagram, see Smith (S. W. J.), *Proc. Physical Soc.*, 1916, 28, 148.

however, has the same concentration as originally. There is clearly some connection between the decrease in concentration of the electrolyte in a compartment and the movement of the ion *leaving* that compartment; in the case considered the anion does not move, hence the cathode compartment remains unchanged. Further, suppose the cations carry two faradays in one direction whilst the anions carry three faradays in the opposite direction; the speeds of the positive and negative ions are in the ratio of 2 : 3, and two cations pass from left to right at the same time as three anions move in the opposite direction. The result is shown in Fig. 2, III; five equivalents of each ion are discharged, as required by the passage of five faradays. The concentration of the anode compartment is reduced from eight to six, i.e. by 2, and that of the cathode compartment from eight to five, i.e. by 3. From this, and from other cases of the same type, it follows that the *reduction* in the number of equivalents of electrolyte in any compartment is proportional to the speed of the ion leaving that compartment. If u is taken as the actual speed of the cations, and v the speed of the anions, for a given electrolyte, then

$$\frac{u}{v} = \frac{\text{Decrease of Concentration of the Anode Compartment}}{\text{Decrease of Concentration of the Cathode Compartment}} \quad (\text{i})$$

This equation involves the assumption that there is a middle compartment (*CD*) which maintains its concentration unchanged; in other words, it is stipulated that the anode and cathode compartments are quite distinct and do not overlap. The 'overlap' might occur if electrolysis were very prolonged, or the solution disturbed.

Transport (or Transference) Number—The quantity of electricity carried by the cations is proportional to their speed u , and the quantity carried by the anions in the opposite direction is proportional to v ; hence the total current carried is proportional to $u + v$. The fraction of the total quantity of electricity carried by the cations is, therefore, equal to $u/(u + v)$; this fraction is called the **transport number**, or **transference number**, of the cation, and is given the symbol n_c . Similarly the transport number of the anion is equal to $v/(u + v)$, and expressed by the symbol n_a ; it is obvious that the sum of n_c and n_a must be unity.

The general case of the concentration changes occurring in an electrolyte MA , giving M^+ and A^- ions with transport numbers n_c and n_a respectively, may now be considered. If one faraday of electricity passes through the cell, n_c faradays are carried by n_c gm. equiv. of cations in one direction, and n_a faradays in the other by n_a gm. equiv. of anions; the following changes then occur:

Anode Compartment.	Middle Compartment.	Cathode Compartment.
1 gm. equiv. of A^- is discharged.	n_c gm. equiv. of M^+ migrate in.	1 gm. equiv. of M^+ is discharged.
n_c gm. equiv. of M^+ migrate out.	n_c gm. equiv. of M^+ migrate out.	n_a gm. equiv. of A^- migrate out.
n_a gm. equiv. of A^- migrate in.	n_a gm. equiv. of A^- migrate in.	n_c gm. equiv. of M^+ migrate in.
	n_a gm. equiv. of A^- migrate out.	

Net Result—

Loss of 1 - $n_a = n_c$ gm. equiv. of A^- .	No alteration.	Loss of 1 - $n_c = n_a$ gm. equiv. of M^+ .
Loss of n_c gm. equiv. of M^+ .		Loss of n_a gm. equiv. of A^- .
i.e. net loss of n_c gm. equiv. of MA.		i.e. net loss of n_a gm. equiv. of MA.

$$\therefore \frac{\text{Decrease of concentration of anode compartment}}{\text{Decrease of concentration of cathode compartment}} = \frac{n_c}{n_a} = \frac{u}{v} \quad (\text{ii})$$

Further,

$$\frac{\text{No. of equivalents of electrolyte lost from anode compartment}}{\text{No. of equivalents of electrolyte lost from both compartments}} = n_c \quad (\text{iii})$$

This may be written in the form :

$$\frac{\text{No. of equivalents lost from anode compartment}}{\text{No. of equivalents deposited on each electrode}} = n_c \quad (\text{iv})$$

Similarly,

$$\frac{\text{No. of equivalents lost from cathode compartment}}{\text{No. of equivalents deposited on each electrode}} = n_a \quad (\text{v})$$

In the experimental determination of transport numbers it is usual to include a coulometer in the circuit so as to determine the number of faradays passing, and thus the number of equivalents deposited at each electrode ; the quantities deposited in the coulometer and in the experimental system must be equivalent. The equation (iv) for the transport number may then be written :

$$n_c = \frac{\text{No. of equivalents lost from anode compartment}}{\text{No. of equivalents of metal deposited in coulometer}} \quad (\text{vi})$$

and similarly for the anion.* In actual practice, since $n_c + n_a$ is equal to unity, only one of these quantities is generally determined.

Transport Numbers in Complex and Mixed Electrolytes—Hitherto a single binary electrolyte, i.e. one yielding only two ions, has been considered ; if the electrolyte contains more

* The number of equivalents lost from a compartment may be expressed in terms of either ion or of the electrolyte, since these quantities are equal.

than two different kinds of ion, as in sulphuric acid solution which contains H^+ , HSO_4^- and SO_4^{--} ions, or in a mixture of two simple salts, each ion will take part in the transfer of current. The quantity of electricity (q_1) which each type of ion is able to carry is proportional to the *equivalent* concentration (c_1) of the particular ion and its velocity (u_1); hence

$$q_1 = k(c_1 u_1).$$

The total quantity of electricity (Q) carried by all the ions in the electrolyte is proportional to the sum of the separate cu terms for all the ions, positive and negative; that is

$$Q = k(c_1 u_1 + c_2 u_2 + c_3 u_3 + \dots) = k \Sigma cu.$$

The transport number (n_1) of any ion, i.e. the fraction of the total current carried by the particular ion is q_1/Q , therefore

$$n_1 = \frac{c_1 u_1}{c_1 u_1 + c_2 u_2 + c_3 u_3 + \dots} = \frac{c_1 u_1}{\Sigma cu}$$

$$\text{and } n_2 = \frac{c_2 u_2}{c_1 u_1 + c_2 u_2 + c_3 u_3 + \dots} = \frac{c_2 u_2}{\Sigma cu}, \text{ etc.}$$

Since cu in general represents the amount of electricity carried by any ion, it is proportional to the number of equivalents of that ion migrating *from* the appropriate compartment, and Σcu is proportional to the number of equivalents deposited in a coulometer. The transport number of any ion is equal to the number of equivalents of that ion migrating from the compartment, divided by the total number of equivalents of metal deposited in the coulometer.*

In deducing the various formulæ it has been assumed that the electrodes are not attacked by the ions liberated, and that the water is not decomposed; when the ions have their charges neutralized, they are therefore considered to be completely removed from the sphere of action, and need not be taken further into account. This is rarely the case, however, and so corrections must be applied. Consider a solution of silver nitrate electrolysed between silver electrodes: when silver ions reach the cathode and are discharged metallic silver is deposited and so removed from the solution. The nitrate ions (NO_3^-), however, cannot be liberated as NO_3 , and so it may be supposed that the discharged radicals immediately attack the silver anode; in this way an amount of silver equal to the

* For further discussion of transport numbers in mixtures, see Mackay, *J. Amer. Chem. Soc.*, 1911, 33, 308; MacInnes, *ibid.*, 1925, 47, 1922; Taylor, *ibid.*, 1926, 48, 599; McBain and van Rysselberghe, *ibid.*, 1931, 52, 2336; van Rysselberghe, *ibid.*, 1933, 54, 990, 996; Longworth, *ibid.*, 1930, 52, 1897; 1935, 57, 1698; Bennowitz, Wagner and Küchler, *Physikal. Z.*, 1929, 30, 623; Onsager and Fuoss, *J. Physical Chem.*, 1932, 36, 2689.

weight of silver deposited at the cathode, or in the coulometer, dissolves into the anode compartment.* In determining the number of equivalents of silver *lost* from the anode compartment, allowance must be made for the amount dissolved off from the anode; if this correction is not made the anode compartment shows an increase of concentration, and the formulæ for the transport numbers are not applicable.

Experimental Determination of Transport Numbers—

The principle of the method devised by Hittorf was to allow a quantity of electricity, determined in a coulometer, or in the apparatus itself by weighing the cathode, to pass through the electrolyte of known concentration; after the passage of current the concentrations of the anode and cathode compartments were re-determined. A middle portion was also taken for analysis, so as to make certain that the concentration had not changed and the anode and cathode compartments were quite distinct. Precautions must always be taken against mixing of the electrolyte as a result of mechanical vibration, of convection currents caused by local heating, or of diffusion. In Hittorf's original work short and wide electrolysing tubes were used, in order to reduce the electrical resistance, and porous partitions were inserted to prevent mixing by diffusion; later, Bein† showed that these partitions modified the speeds, and hence the transport numbers, of the ions and so special apparatus has been designed in which mixing is avoided without the use of membranes.

One of the simplest types of transport number apparatus, giving results of fair accuracy if care is exercised in manipulation, was used by Nernst and Loeb‡ in their work on silver nitrate. The apparatus, which holds 40 to 60 c.c., is shown diagrammatically in Fig. 3. The anode *A* is a thick silver wire, sealed into a glass tube; it is placed in the longer arm of the vessel, as the concentration at the anode increases and the solution will tend to sink. The cathode *B* is of silver wire or foil. The apparatus is filled with the experimental solution of known concentration and it is then placed in a thermostat; the electrodes are connected in series with a copper or silver coulometer, and a small current (0.01 amp.) is passed for two or three hours. Too long a time must not be used otherwise the results will be vitiated by diffusion, and too large a current will produce mixing by convection due to heating. At the end of the experiment the anode liquid, from *a* to *b*, is forced out through the side-tube *C* by blowing gently through the tube *D*; this solution is weighed and analysed. Another portion, from

* Although there is no certainty as to the exact mechanism of the anode reaction, there is no doubt about the final result.

† *Z. physikal. Chem.*, 1899, 28, 439.

‡ *Ibid.*, 1888, 2, 948.

b to *c*, is also removed in the same way and analysed; this corresponds with the 'middle compartment', and its concentration should remain unchanged. The amount of metal deposited in the coulometer during the passage of the current is also determined.*

Calculation of Transport Numbers from Experimental

Results—The following example, taken from the results of Nernst and Loeb, indicates the method of calculation. Before the experiment 1 gm. of the anode solution contained 0.001788 gm. of silver nitrate, i.e. 0.001139 gm. silver; after the experiment 20.09 gms. of solution taken from the anode compartment were found to contain 0.06227 gm. silver nitrate, i.e. 0.03966 gm. silver. During electrolysis 0.0322 gm. silver was deposited in a coulometer. As a silver anode had been used an equal amount (0.0322 gm.) must have dissolved off into the anode solution, and allowance has to be made for this in determining the *fall* of concentration in the anode compartment.

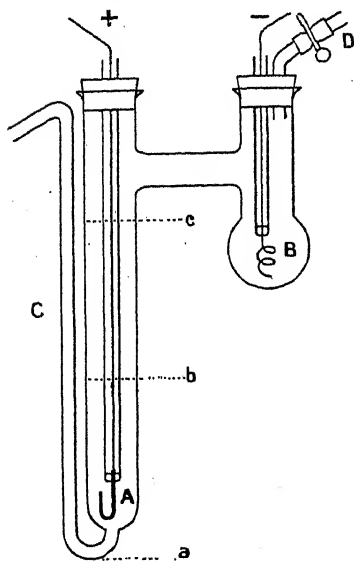


FIG. 3.—Transport number apparatus

After the experiment $20.09 - 0.06227 (= 20.03)$ gms. water are associated with 0.03966 gm. silver.

Before the experiment $1 - 0.001788 (= 0.9982)$ gm. water was associated with 0.001139 gm. silver.

\therefore 20.03 gms. water were originally associated with

$$\frac{0.001139 \times 20.03}{0.9982} = 0.02285 \text{ gm. silver.}$$

Hence *increase* of amount of silver in anode compartment

$$= 0.03966 - 0.02285 = 0.01681 \text{ gm.}$$

* In the form of apparatus used in general laboratory work the side tube *C* is replaced by a tap at the bottom of the anode compartment; the anode liquid is run gently out of this at the end of the experiment. This apparatus cannot, however, be used in an ordinary thermostat. As it is not necessary in this particular experiment to analyse the cathode solution, the silver cathode is frequently replaced by one of copper and a concentrated solution of copper nitrate acts as cathode electrolyte; the right-hand side of the apparatus (Fig. 3) is then made rather deeper than is shown in the diagram. For details see text-books of practical physical chemistry.

But 0.0322 gm. silver had been dissolved off from the anode itself, and if this had not occurred the compartment would have *lost*

$$0.0322 - 0.01681 = 0.01541 \text{ gm. silver.}$$

$$\begin{aligned} \text{Since } n_c &= \frac{\text{Loss of silver from anode compartment}}{\text{Total wt. of silver deposited in coulometer}} \\ &= \frac{0.01541}{0.0322} = 0.478, \end{aligned}$$

$$\text{then } n_n = 1 - n_c = 0.522.$$

The transport numbers of the silver and nitrate ions are 0.478 and 0.522 respectively in the solution examined; the nitrate ion, therefore, carries a larger proportion of the current and has a greater velocity than the silver ion.*

Other Types of Apparatus—Since the original investigations of Hittorf much work has been done on the subject of transport numbers † by the method involving the determination of concentration changes in the vicinity of the electrodes. Although the principle of the method has remained unchanged various improvements have been made in the apparatus. Ground-glass plugs have been used to separate anode and cathode compartments at the end of the experiment,‡ and wide stop-cocks have been employed for the same purpose;§ Noyes|| used an apparatus consisting of two U-tubes connected together and was thus able to add acid or alkali to the electrolyte through the open ends of the tubes in order to keep the solution neutral; runs of seven hours duration were made with this apparatus and comparatively large currents were used. In order to prevent diffusion from one compartment to another, a U-tube has been introduced between anode and cathode sections; ** this U-tube is regarded as the middle compartment and the concentration of electrolyte in it must remain unchanged. With certain solutions, e.g. hydrochloric acid and alkali halides, there is a possibility of the liberation of gases at one or both electrodes, and

* For examples of different types see Knox, *Physico-chemical Calculations*, pp. 119, 135; Partington and Tweedy, *Calculations in Physical Chemistry*, pp. 98, 99.

† For reviews and references, see McBain, *Proc. Wash. Acad. Sci.*, 1907, 9, 1; Noyes and Falk, *J. Amer. Chem. Soc.*, 1911, 33, 1436; Taylor, *Physical Chemistry*, 1931, p. 680 (Partington); Walden, *Das Leitvermögen der Elektrolyte*, 1924, Vols. I and II.

‡ e.g. Hopfgartner, *Z. physikal. Chem.*, 1898, 25, 115; Jahn, *ibid.*, 1901, 37, 673.

§ Hellwig, Rieger and Mather, *Amer. Chem. J.*, 1901, 26, 473; Jones (H. C.) and Bassett (H. P.), *ibid.*, 1904, 32, 409; Washburn, *J. Amer. Chem. Soc.*, 1909, 31, 322; MacInnes and Dole, *ibid.*, 1931, 53, 1357. || *Z. physikal. Chem.*, 1901, 36, 63; *J. Amer. Chem. Soc.*, 1901, 23, 148.

** Jones and Bassett, *loc. cit.*; Findlay, *Chem. News*, 1900, 120, 185; Getman, *J. Amer. Chem. Soc.*, 1914

thus stirring may be caused and vitiate the experiment. Hittorf* used a cadmium anode which was attacked by the discharged chlorine and so the liberation of gas was prevented. The evolution of hydrogen is avoided by the use of a mercury cathode covered with a solution of zinc chloride or copper nitrate.† When working with solutions of alkali chlorides silver anodes, which form insoluble silver chloride, have been used to avoid evolution of chlorine, and silver cathodes coated with silver chloride have been employed to prevent hydrogen gas being evolved.‡ Apart from the mixing effect of gas evolution the accompanying formation of acid and alkali (p. 12) has a complicating influence, and hence must be avoided.§

The Moving Boundary Method ||—The idea of measuring ionic velocities by observations of a moving boundary was first used by Lodge,** who endeavoured to follow the movements of certain ions by means of their reactions with chemical indicators. Thus the passage through a tube, filled with conducting gelatine, of barium and chlorine ions was followed by the faint cloudiness caused by each ion reacting with a trace of silver sulphate contained in the gelatine. Whetham†† avoided the use of conducting gels and observed the movement of the boundary between two electrolytes, one of which had a coloured ion to act as indicator; incidentally Whetham first realized the conditions necessary for obtaining a sharp boundary. In 1899 Masson‡‡ combined the methods of Lodge and of Whetham, and determined the rate of movement through a conducting gel of the boundary between a coloured and a colourless ion; this method was claimed to give accurate results for the absolute speeds of both ions in one electrolyte, and could, therefore, be used for transport number measurements. Steele§§ showed that the movement of the boundary in the conducting gel could be avoided by the use of such a gel for the indicator solution only; in this way a sharp boundary was obtained, but the effect of the gel on its movement was eliminated. By making use of the

* *Ann. Physik*, 1858, 103, 1.

† Hopfgartner, *loc. cit.*; Jahn, *loc. cit.*; Birkenstock, *Z. physikal. Chem.*, 1928, 138, 432.

‡ Noyes and Sammet, *J. Amer. Chem. Soc.*, 1902, 24, 947; Washburn, *loc. cit.*; Jones (G.) and Dole, *ibid.*, 1929, 51, 1073.

§ For full description of various types of transport number apparatus see Arndt, *Handbuch der Physikalisch-Chemischen Technik*, Chap. 25; see also Taylor, *Physical Chemistry*, 1931, p. 681 (Partington).

|| For review article, see MacInnes and Longworth, *Chem. Reviews*, 1932, 11, 171.

** *Brit. Assoc. Reports*, 1886, p. 389.

†† *Phil. Trans.*, 1893, 184 A, 337; 1895, 186 A, 507.

‡‡ *Ibid.*, 1899, 192 A, 331.

§§ *J. Chem. Soc.*, 1901, 79, 414; *Phil. Trans.*, 1902, 198 A, 105.

differences in refractive index of the solutions the motion of the boundary between two colourless electrolytes could be followed, and so the use of solutions with coloured ions was no longer necessary. A light was placed behind the tube containing the boundary and the movement was easily followed by means of a cathetometer. The transport numbers of ions were determined for a few solutions, but the results were not in good agreement with those of Hittorf. Later Denison and Steele* improved the apparatus so that conducting gels were not used at all, and possible errors due to endosmose were avoided. The denser electrolyte was always placed below the lighter and special precautions were taken to get a sharp boundary. Transport numbers and absolute velocities of several ions were determined with a supposed accuracy of one part in 300; it was claimed that with a dilute solution the determination could be completed in half an hour. The moving boundary method has recently been modified and much improved by MacInnes and his co-workers, so that very accurate results are easily obtained.

Theory of Moving Boundary Method—

Before describing the experimental method in detail the theory of the process must be discussed. If a salt MA (e.g. potassium chloride) is to be studied two other salts M'A and MA' (e.g. lithium chloride and potassium acetate), each having an ion in common with the first salt, are required to form the boundaries. The solution of MA is then placed in between the solutions of the other two salts (see Fig. 4); the latter are known as the 'indicator solutions'. If possible the three solutions are arranged in order of increasing density downwards in order to avoid mixing due to gravitational effects. The anode is placed in the indicator solution M'A, and the cathode in the solution of MA'. In order that the boundaries *a* and *b*, between M'A and MA, and between MA and MA', respectively, may remain distinct the first requirement is that the speed of the ion M' should be less than that of M, and the speed of A' less than that of A; if these conditions hold then M' ions do not overtake the M ions at *a*, neither do the A' ions overtake the A ions at *b*, and the boundaries do not become blurred. Under the in-

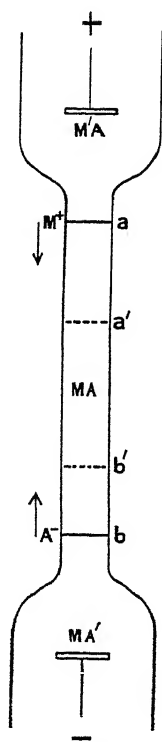


FIG. 4.—The principle of the moving boundary method

* *Ibid.*, 1906, 205 A, 449.

fluence of the electric field the boundary a moves to a' in a given time, whilst the boundary b moves to b' ; the distances aa' and bb' must depend on the speeds of the ions M and A respectively. The actual speed of an ion is proportional to the fall of $E.M.F.$, or potential gradient, through the solution (p. 74), and this gradient depends on the resistance. Since the solution MA in the experiment is homogeneous its resistance must be the same throughout, and so the fall of potential must be uniform along the whole of its length. The M and A ions are, therefore, moving under the influence of the same applied potential; hence the distances aa' and bb' are directly proportional to the speeds of the ions M and A, respectively, i.e. to u and v . It follows, then, that

$$u + v = \frac{aa'}{aa' + bb'} \quad \dots \quad (vii)$$

and similarly,
$$n_a = \frac{bb'}{aa' + bb'} \quad (viii)$$

To obtain sharp moving boundaries it is obviously necessary that the cations M and M' should move with almost exactly the same speeds, and that the anions A and A' should also have equal speeds, under the conditions of the experiment. It can be readily shown* that if the relationship

$$\frac{n}{c} = \frac{n'}{c'} \quad \dots \quad (ix)$$

where c and c' are the concentrations of the ions not in common at a boundary, and n and n' their respective transport numbers, hold good then the required conditions for a sharp moving boundary are satisfied. The adjustment of the concentration of the indicator solutions, to agree with this relationship, makes their resistances such that the potential gradients in the three solutions are exactly those required to equalize the speeds of the ions M and M' at one boundary, and the speeds of the ions A and A' at the other. It should be made quite clear that the solution of MA remains homogeneous between the boundaries a' and b' , and so the M and A ions are moving under the same potential gradient.

Adjustment of Indicator Concentration—If one faraday of electricity flows between two electrodes one gm. equiv. of each ion is liberated, and n_o gm. equiv. of the cation must pass any given point in one direction whilst n_a gm. equiv. of anion pass in the opposite direction. Suppose ϕ is the volume of solution containing

* Kohlrausch, *Ann. Physik*, 1897, 62, 209; see also Masson, *loc. cit.*; Denison, *Z. physikal. Chem.*, 1903, 44, 581; Miller, *ibid.*, 1909, 69, 436; von Laue, *Z. anorg. Chem.*, 1915, 93, 329. For the behaviour in a mixed solution of two electrolytes with a common ion, see Longworth, *J. Amer. Chem. Soc.*, 1930, 52, 1897.

1 gm. equiv. of electrolyte, then during the passage of one faraday, i.e. $F (= 96,500)$ coulombs, the cation boundary must sweep through a volume equal to ϕn_c ; for the passage of Q coulombs the cation boundary must, by proportion, move through a volume $Q\phi n_c/F$. This relationship applies equally to leading and following ions at a given boundary, and since Q is the same for both ions, it is evident that

$$\phi n = \phi' n'$$

where ϕ and n apply to one ion and ϕ' and n' to the other. Since ϕ , the volume containing 1 gm. equiv. of electrolyte, is inversely proportional to its concentration c , it follows that

$$n/c = n'/c'$$

where c and c' refer to the two solutions constituting the boundary. This expression is identical with equation (ix) which gives the Kohlrausch 'regulating function' for a sharp boundary. It appears, therefore, that the requisite condition should be established automatically in the vicinity of the boundary soon after current begins to pass, and consequently the actual concentration of the bulk of the indicator solution should be immaterial.* In actual practice, however, it has been found † that the measured transport numbers do in fact depend on the concentration of the bulk of the indicator solution. This departure from the behaviour expected theoretically is probably due to the disturbing effect of convection, resulting from temperature and concentration gradients in the electrolyte.‡ The values for the transport number of the potassium ion in 0.1N-potassium chloride solution at 25°, using different concentrations of lithium chloride as indicator,§ are given in Table III.

TABLE III

TRANSPORT NUMBER OF POTASSIUM ION IN 0.1N-POTASSIUM CHLORIDE, WITH LITHIUM CHLORIDE AS INDICATOR SOLUTION

Conc. of Lithium Chloride	Transport Number of Potassium Ion.	
0.1N	0.507	0.507
0.0887	0.497	0.498
0.08	0.494	0.496
0.075	0.493	0.494
0.07	0.492	0.492
0.065	0.491	0.492
0.06	0.491	0.493
0.055	0.493	0.497
0.035	0.489	0.489

* This does not, however, rule out the necessity of having an indicator ion with a speed smaller, under similar conditions, than that of the ion being studied.

† MacInnes and Smith (E. R.), *J. Amer. Chem. Soc.*, 1923, **45**, 2246; see also Mukherjee *et al.*, *J. Indian Chem. Soc.*, 1936, **13**, 42.

‡ Hartley (G. S.) and Moilliet, *Proc. Roy. Soc.*, 1933, **140 A**, 141.

§ MacInnes and Smith, *loc. cit.*

As the indicator solution decreases in concentration the transport number appears to decrease first and then increase; over the range 0.075 to 0.055*N*-lithium chloride the value of the transport number is almost constant at 0.492. This, incidentally, appears to be the correct value. From the known transport numbers of potassium and lithium in their respective chlorides, obtained by the Hittorf method, the ideal concentration of lithium chloride, according to the equation $n/c = n'/c'$, should be 0.064*N*. It appears, therefore, that automatic adjustment of concentration at the boundary does not occur unless the original concentration of the indicator solution is in the vicinity of the ideal concentration.* In actual practice the bulk concentration of the indicator should be chosen so as to comply with equation (ix), approximate transport numbers being used in the calculation. The transport number should then be measured and the experiment repeated with an indicator solution of slightly different concentration. The procedure should be continued until a constant value for the transport number is obtained; this value must be independent of the nature of the indicator, and of the strength of the current passing through the apparatus, i.e. of the potential gradient. Only when the concentration of the indicator solution is correctly adjusted is the transport number quite independent of the applied *E.M.F.*†

migration; * the equation for transport number then becomes

$$n_c = \frac{1}{\phi} \left(\frac{laF}{Q} + \Delta v \right) \quad \dots \dots \dots (xi)$$

where Δv is the increase of volume at the cathode per faraday.† Since part of the current is carried by the solvent itself, and by impurities which it may contain, it is necessary to employ a 'solvent correction'; this correction is applicable also to the Hittorf method for measuring transport numbers and is appreciable in dilute solutions only, provided the solvent has little conductivity. Longworth‡ has shown that the observed transport number may be corrected by means of the equation

$$n_{\text{corr.}} = n_{\text{obs.}} \left(1 + \frac{\kappa_0}{\kappa_s} \right)$$

where $n_{\text{corr.}}$ and $n_{\text{obs.}}$ are the corrected and observed transport numbers, and κ_0 and κ_s are the 'specific' conductivities (see p. 55) of the pure solvent and the solution in which the transport number is being measured, respectively.

Experimental Method—

Since one boundary only is generally observed, it is sufficient to employ one indicator solution, and this must have an ion in common with the experimental solution but opposite in sign to the one being studied. When measuring the transport number of the potassium ion in potassium chloride, for example, lithium chloride may be used as indicator. An early form of the apparatus used by MacInnes and Smith§ is shown diagrammatically in Fig. 5; the indicator solution was contained in A, B and F, and the solution under examination in C and D, the flat rubber disc, shown at F, keeping the two electrolytes separated.

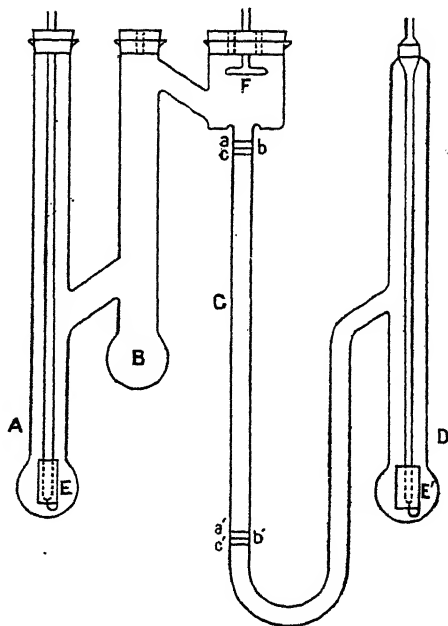


FIG. 5.—Moving boundary apparatus

* Lewis (G. N.), *J. Amer. Chem. Soc.*, 1910, **32**, 862.

† See Smith (E. R.), *Bur. Stand. J. Res.*, 1932, **8**, 457.

‡ *J. Amer. Chem. Soc.*, 1932, **54**, 2741.

§ *ibid.*, 1924, **46**, 1398; 1925, **47**, 1009.

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$$n_c = \frac{I}{\phi} \left(\frac{laF}{Q} + \Delta v \right) \quad \dots \dots (xi)$$

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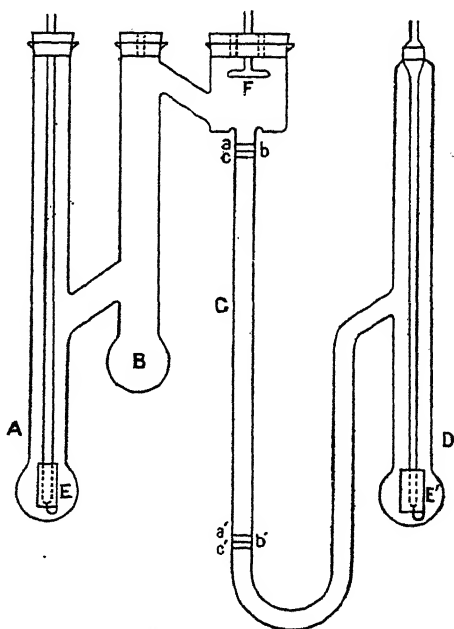


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‡ *J. Amer. Chem. Soc.*, 1932, 54, 2741.

§ *ibid.*, 1924, 46, 1398; 1925, 47, 1009.

The Balanced Boundary Method—An interesting modification of the moving-boundary procedure has been described under the title of the 'balanced boundary' method; it was devised especially with the object of studying the transport numbers of large ions of low speed, but it appears to be equally applicable to other ions. Since the indicator ion must be one which moves more slowly than the ion being studied, it is evident that in certain instances, e.g. for very slowly moving ions, it may not be possible to obtain a suitable indicator solution. In the balanced boundary method it is the transport number of the indicator ion, the slower one, which is actually determined, use being made of the Kohlrausch 'regulating function', equation (ix). If the transport number of the leading ion, e.g. potassium in potassium chloride, is known, and the concentration of the indicator solution, e.g. lithium chloride, in the vicinity of the boundary can be measured, then it is possible to calculate the transport number of the more slowly moving, i.e. lithium, ion. The determination of the concentration of the 'Kohlrausch solution' is obviously not an easy matter, but the difficulty has been overcome in an ingenious manner.* The leading and indicator solutions are first separated by means of a small air bubble trapped at a constriction in the tube in which the boundary is to move: by a simple movement the bubble is ejected and a sharp boundary forms. The current is switched on and the boundary moves downwards for about 3 cms. By means of a piston, the following (indicator) solution which has entered the tube and has the Kohlrausch concentration, is now very gently expelled, so as to avoid mixing effects, into a side tube where its concentration is determined by measuring the conductivity. The transport number can then be calculated by equation (ix) if the concentration and transport number of the leading ion are known.

Results of Transport Number Measurements—In the first place it must be mentioned that provided the experiments are carried out with care both Hittorf and moving-boundary methods give identical results, and so all the data may be considered together. It should be made clear that the transport number of an ion is not a definite constant, but depends on the other ion with which it is associated; the transport number of an ion is equal to the ratio of its own speed (u or v) to the sum of the speeds of both ions ($u + v$). The transport numbers for the two ions of a given electrolyte should of course add up to unity: this has been verified in a number of cases.† In his early work Hittorf investigated the effect of current

* Hartley (G. S.) *et al.*, *Trans. Faraday Soc.*, 1934, 30, 648; 1936, 32, 795.

† MacInnes and Longworth, *loc. cit.*; Longworth, *J. Amer. Chem. Soc.*, 1935, 57, 1185.

strength, and hence applied *E.M.F.*, on the transport number; he found that within the limits of experimental error it was independent of the potential gradient between the electrodes. The factor of current strength and applied voltage can, therefore, be neglected, and other factors, e.g. concentration of the electrolyte and temperature, considered.

Transport Number and Temperature—Since the speed of an ion is probably affected by temperature, and different ions may be influenced to different extents, it is reasonable to expect that the transport number of an ion will vary with temperature. Table IV contains results for cation transport numbers taken from International Critical Tables, Vol. VI, pages 309–10; the concentration of each solution is 0.01*N*.

TABLE IV
VARIATION OF CATION TRANSPORT NUMBERS WITH TEMPERATURE
0.01*N*-SOLUTIONS

Temperature.	NaCl.	KCl.	HCl.	BaCl ₂ .
0°	0.387	0.493	0.846	0.437
10°	—	0.495	0.840	—
18°	0.397	0.496	0.833	—
30°	0.404	0.498	0.822	0.444
50°	—	—	0.801	0.475
96°	—	—	0.748	—

For the ions of potassium chloride the transport number varies very little with the temperature, but in sodium chloride there is an appreciable change. The results indicate that if the transport number is greater than 0.5 an increase of temperature decreases the value, e.g. hydrogen ion in hydrochloric acid; but if it is less than 0.5 it is increased by raising the temperature, e.g. cations in sodium and barium chlorides. It has been found that in general for uni-univalent electrolytes, at least, as the temperature increases the transport numbers of anions and cations alike approach 0.5 in value; this means that all ions tend towards equal speeds as the temperature is raised.*

Transport Number and Concentration—The variation of the transport number with concentration was realized by Hittorf and is in harmony with the requirements of the modern theories of strong electrolytes (Chapter VII). Some results, taken from the International Critical Tables, are given in Table V; † the values are of cation transport numbers at 18°.‡ The transport number

* Kohlrausch, *Sitz. der Berl. Akad.*, 1902, 26, 572.

† For a discussion and critical survey of transport, or transference, number measurements, see Noyes and Falk, *J. Amer. Chem. Soc.*, 1911, 33, 1436.

‡ Results obtained at 25° by the moving-boundary method are recorded by Longworth, *loc. cit.*, p. 1191.

of the anion may be obtained in each case by subtracting the cation transport number from unity.

TABLE V
CATION TRANSPORT NUMBERS AT 18°

Electrolyte.	Concentration. Gm. Equivs. per Litre.							
	0.005	0.01	0.02	0.05	0.1	0.2	0.5	1.0
Lithium Chloride . . .	—	0.332	0.328	0.320	0.313	0.304	—	—
Sodium Chloride . . .	0.397	0.397	0.396	0.393	0.390	0.385	0.374	0.365
Sodium Bromide . . .	0.395	0.395	0.395	—	—	—	—	—
Potassium Chloride . . .	0.496	0.496	0.496	0.496	0.495	0.494	0.492	0.490
Potassium Bromide . . .	—	0.495	0.495	—	—	—	—	—
Hydrochloric Acid . . .	0.832	0.833	0.833	0.834	0.835	0.837	0.838	0.844
Sodium Sulphate . . .	—	0.392	0.390	0.383	—	—	—	—
Barium Chloride . . .	—	—	—	—	0.421	0.409	0.392	—
Cadmium Chloride . . .	0.438	0.430	0.422	0.411	0.402	0.393	—	—
Cadmium Iodide . . .	0.445	0.444	0.442	0.396	0.296	0.127	0.003	—
Copper Sulphate . . .	—	—	0.375	0.375	0.373	0.361	0.327	—
Barium Nitrate . . .	—	—	—	0.456	0.456	0.456	—	—
Lead Nitrate . . .	—	—	—	0.487	0.487	—	—	—

In fairly dilute solutions the variation of transport number with concentration may be expressed by an equation of the form *

$$n = n_0 - A\sqrt{c} \quad \text{. (xii)}$$

where n is the transport number at the concentration c ; A is a constant and n_0 represents the transport number at zero concentration, that is at infinite dilution. Another empirical equation

$$n = \frac{A}{1 + B\sqrt{c}} - 1 \quad \text{. (xiii)}$$

was proposed by Jones (G.) and Dole,† where A and B are parameters chosen to fit the observed results; if the relationship holds in dilute solution then A is equal to $n_0 + 1$, so that there is really only one arbitrary parameter. The equation is applicable to a number of cases,‡ although with lanthanum chloride it is not adequate and further parameters must be introduced.§ Dole|| has shown that the equation (xiii) of Jones and Dole may be deduced from the Debye-Hückel-Onsager relationship, which is based on the newer theories of electrolytic dissociation (Chapter VII), and so may be supposed to have a theoretical basis. It is unfortunate,

* Scatchard, *ibid.*, 1925, 47, 696; see also Drucker and Riethof, *Z. physikal. Chem.*, 1924, 111, 20.

† *J. Amer. Chem. Soc.*, 1929, 51, 1073.

‡ Jones (G.) and Dole, *loc. cit.*; Jones and Bradshaw, *ibid.*, 1932, 54, 138.

§ Jones and Prendergast, *ibid.*, 1936, 58, 1476.

|| *J. Physical Chem.*, 1931, 35, 3647.

however, that the parameters expected theoretically are not in agreement with those found empirically. For dilute solutions it can be seen that the Jones-Dole equation reduces to the simple form of equation (xii). Another relationship having a semi-theoretical basis has been derived by Longworth* from an empirical modification of the Onsager equation; † it is, however, more complicated than those already given as it involves two arbitrary parameters, in addition to the transport number at infinite dilution, although it reduces to the simple equation (xii) at low concentrations.

Causes of Variation of Transport Numbers—The variation of transport number with concentration may be due to a number of different factors. In the first place, it will be seen later (Chapter VII) that ionic velocities are dependent on the concentration of the solution, and if the changes are different for the two ions the transport numbers will alter. The effect is then due to the mutual electrical interaction of the ions, and will clearly be more marked in concentrated solutions. Secondly, it has been suggested that the ions carry a certain amount of water with them; hence there results a change of concentration of the solution in the vicinity of the electrodes which affects the measured transport number. If the transfer of water with the ions varies with the concentration of the solution there will be a corresponding variation in the transport number. This factor probably accounts for small changes, and will be considered in the next chapter.

Abnormal Transport Numbers—In those cases in which the transport number varies considerably with the concentration, e.g. cadmium iodide, it is very probable ‡ that complex or intermediate ions are present in the electrolyte at the higher concentrations. Not only may these ions have different velocities from the simple ions, but a complex anion generally contains the metal which would normally be the cation, e.g. $\text{Ag}(\text{CN})_2^-$, CdI_4^{--} ; the metal, e.g. silver, or cadmium, is thus carried *towards* the anode instead of *away* from it. As the solution is diluted the complex ion usually dissociates into simpler ions, and so the transport number changes and eventually reaches a constant value for the simple ions of the electrolyte. The case of cadmium iodide was studied by Hittorf, who found that in a concentrated solution the transport number of the anion was actually greater than unity; at first sight this appears to imply that the anion is carrying more current than is actually passing through the solution! The anomalous result can best be accounted for by assuming that a complex anion (CdI_4^{--}) containing cadmium is formed, and so the cathode compartment is

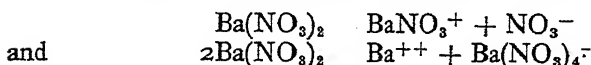
* *J. Amer. Chem. Soc.*, 1932, 54, 2741.

† Shedlovsky, *ibid.*, p. 1405.

‡ Hittorf, *Ann. Physik.*, 1859, 106, 337, 513.

depleted of this element by transport to the anode; the speed of the anion, which is proportional to the decrease in concentration of the cathode compartment, would thus appear to be abnormally large. If it is assumed then that a concentrated solution of cadmium iodide contains not merely Cd^{++} and I^- ions, but mainly Cd^{++} and CdI_4^{--} ions, it is seen that cadmium is transported both into and out of the anode compartment; and so there may well be an actual *gain* in the cadmium concentration. This would give an *apparent* negative value for the transport number of the cation, and a value greater than unity for the anion. The marked variation in the measured transport number of cadmium iodide with concentration (Table V) suggests that complex formation is considerable at higher concentrations, but decreases as the solution is made more dilute; in a 0.01*N*-solution only simple ions appear to exist. Similar variation of the transport number with concentration of the electrolyte, although not so marked, has been observed with other salts which probably contain complex anions in concentrated solution.*

Just as the presence of complex anions makes the apparent anion transport number too large, complex cations would have the effect of making it too small. If both complex anions and cations are present in similar amounts the transport number may remain constant as the concentration is changed; this probably occurs with barium nitrate. The cation transport number of this electrolyte is apparently constant between 0.05*N* and 0.2*N* (Table V); such a result is not to be expected for a ternary electrolyte ionizing in stages.† It is possible, therefore, that concentrated solutions of barium nitrate may contain the complex cation BaNO_3^+ , and the complex anion $\text{Ba}(\text{NO}_3)_4^{--}$; the apparent cation transport number would be affected in opposite directions. Thus:



With increasing dilution both complex ions would tend to dissociate into simple ions, and their mutually exclusive influences on the measured transport number would continue. It is not to be expected that the effect of the complex cation would always counteract exactly the effect of the anion; hence some change of transport number with dilution, especially in very dilute or very concentrated solutions, is to be anticipated.

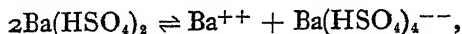
The apparent transport number of the barium ion in a solution of barium bisulphate in anhydrous sulphuric acid is less than 0.01,‡

* See, for example, Cantelo and Payne, *J. Physical Chem.*, 1932, 36, 1045.

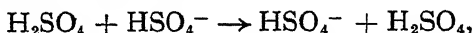
† Cf. Noyes, *Z. physikal. Chem.*, 1901, 36, 63.

‡ Hammett and Lowenheim, *J. Amer. Chem. Soc.*, 1934, 56, 2620.

and at first sight it appears that a complex anion is formed, as with cadmium iodide in aqueous solution, thus :

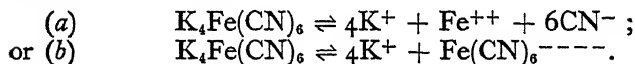


but freezing-point measurements * rule out this explanation. It is possible that the velocity of the bisulphate ion may be very high in comparison with that of the barium ion, but the value required to account for the observed conductivities would have to be much greater than is probable for a medium as viscous as sulphuric acid. It appears that in the solution under consideration the conduction does not depend on simple ionic migration, but may be due to a phenomenon analogous to a Grotthuss chain (p. 14): if protons, that is bare hydrogen ions, are passed from sulphuric acid molecules to bisulphate ions, thus :



the electrolytic conduction without ionic transport can be explained. Grotthuss conduction has also been proposed to account for the apparently high transport number of hydrogen ions in aqueous solutions (see p. 86).

Formulae of Complex Ions—A certain amount of information concerning the formulae of complex ions may be obtained from transport measurements. For example, potassium ferrocyanide is known by analysis to have the formula $\text{K}_4\text{Fe}(\text{CN})_6$; this may ionize in two ways :



By electrolysis a solution of potassium ferrocyanide between platinum electrodes, and analysing the anode and cathode compartments before and after the experiment, it may be shown (i) that all the iron migrates to the anode, and hence is present as a complex anion, and (ii) six CN radicals migrate with every Fe atom. These results favour the (b) method of ionization, and indicate the complex ferrocyanide ion to be $\text{Fe}(\text{CN})_6^{----}$.† This method is only applicable if the complex ion is a stable one, and the solution does not contain any appreciable concentration of the simple ions making up the complex. If the current is carried by several ions the results are very difficult, if not impossible, to interpret quantitatively.‡

Another example is taken from the work of Whitney and Mel-

* Hammett and Deyrup, *ibid.*, 1933, 55, 1900.

† The discussion of this subject by Hittorf, cf. Jacques, *Complex Ions*, 1914, p. 14, does not appear to be rigid.

‡ For other examples, see Lorenz and Posen, *Z. anorg. Chem.*, 1916, 95, 340; 1916, 96, 81; Duval, *Compt. rend.*, 1935, 200, 2175.

cher * on the complex argentammine cations, $\text{Ag}(\text{NH}_3)_x^+$. When ammonium hydroxide is added in excess to a solution of silver nitrate, the only cations which can carry the current are those of the argentammine complex; the ammonium hydroxide is only slightly dissociated, and so contributes very few NH_4^+ ions, whereas the silver ions are removed to form the complex. Suppose such a solution is placed in the anode compartment and the rest of the vessel filled with sodium nitrate solution, then if only one *stable* complex ion is formed, the analysis, after electrolysis, of portions of the solution at various distances from the anode compartment should give information concerning the composition of the complex. The result of such experiments was to show that the ratio of NH_3 to Ag was always approximately 2 to 1, although the ratio in the original anode solution varied from 2.5 : 1 to 3.5 : 1. This indicates that all the silver is present in the form of a complex positive ion $\text{Ag}_n(\text{NH}_3)_{2n}$. Had the complex ion been unstable, so that part of the current was carried by silver ions, this method would have been unsatisfactory.

Applications of Ionic Migration †—In the technical alkali-chlorine cells a solution of sodium or potassium chloride is electrolysed between electrodes separated by a porous diaphragm; alkali hydroxide is formed at the cathode and chlorine is liberated at the anode. As the hydroxide accumulates it begins to take part in conducting the current, and hydroxyl ions move, together with chlorine ions, towards the anode. In the anode compartment they may react with the liberated chlorine gas or with hydrogen ions, which are there present in excess, so that the yield of alkali and of chlorine may be markedly decreased. It is found, however, that with potassium chloride the yields are greater than with the sodium salt, working under exactly the same conditions; the explanation is to be found in the difference of ionic velocity. The transport number of the hydroxyl ion in sodium hydroxide is 0.83, but in potassium hydroxide it is 0.74; hence under equivalent conditions a greater proportion of the current will tend to be carried by the hydroxyl ions during the electrolysis of sodium chloride than of potassium chloride. In the former case, therefore, more hydroxyl ions leave the cathode compartment and enter the anode section, and so the yield of alkali and of chlorine is lower than in the latter. It should be mentioned that the diaphragm affects the transport numbers of both hydroxides approximately to the same extent. An increase of temperature decreases the transport number of the

* *J. Amer. Chem. Soc.*, 1903, 25, 69. See also Wille, *Z. physikal. Chem.*, 1934, 171, 93 for copper-amine complexes.

† For technical aspects, see Allmand and Ellingham, *Applied Electrochemistry*, 1924, p. 410 *et seq.*

hydroxyl ion and so improves the yield of alkali hydroxide. In order to overcome, to some extent, the effect of migration in reducing the yield, cells with moving electrolytes have been devised, e.g. 'Bell-jar' and Billiter cells; in these fresh chloride solution is caused to flow in the opposite direction to that in which the hydroxyl ion migrates, i.e. from anode to cathode compartments.

Separation of Elements from one another—An attempt has been made to separate the isotopes of lithium and of chlorine by the use of the principle of the moving boundary; if the isotopic ions had different mobilities, corresponding with differences of mass, a separation might be possible. The method used* was to place a long tube containing sodium chloride in an agar gel, between tubes containing sodium hydroxide and sodium acetate, respectively, in agar. The velocities of the anions are in the order: hydroxyl > chlorine > acetate, hence if the anode is placed at the sodium hydroxide end and the cathode at the acetate end, the ions are in the correct order for giving sharp boundaries. When the chlorine ion boundary has moved to the end of its tube, the chloride is now wholly in the tube originally containing hydroxide. The middle tube is then removed, replaced by the hydroxide tube, a new hydroxide tube connected up and electrolysis started once more. By this means the chlorine ion has been made to travel through 100 ft. of gel, and if there had been present a faster-moving isotopic ion it would have been found in excess in the front part of the tube containing chloride. So far no separation has been detected, and it is even doubtful if the method can ever be successful.† The same principle has, however, been used to accomplish a complete separation of sodium iodide from thiocyanate, and sodium iodide from chloride, although the speeds of the anions are very little different.‡ A separation of yttrium from a mixture of rare-earth salts, of hafnium from zirconium, and the removal of radium and meso-thorium from barium have been achieved by the moving-boundary method.§

* Kendall and Crittenden, *Proc. Nat. Acad. Sci.*, 1923, 9, 75.

† See Pilley, *Phil. Mag.*, 1925, 49, 889; Jette, *ibid.*, 1927, 3, 258.

‡ Kendall and White, *Proc. Nat. Acad. Sci.*, 1924, 10, 458.

§ Kendall and Clarke, *ibid.*, 1925, 11, 393; Kendall and West, *J. Amer. Chem. Soc.*, 1926, 48, 2619; Kendall, West and Jette, *ibid.*, p. 3114.

CHAPTER III

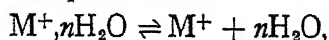
THE HYDRATION (SOLVATION) OF IONS

TRUE Transport Numbers and the Hydration of Ions
 —The transport numbers of the cations in 0.05*N*-solutions of the alkali metal chlorides at 18° are as follows:

Lithium chloride	0.320
Sodium ,,	0.386
Potassium ,,	0.496
Rubidium ,,	0.485
Cæsium ,,	0.492

These results are quite unexpected as it would be anticipated that the lightest ion, viz. lithium, would have the highest velocity, and the heaviest ion, cæsium, the smallest. In order to explain this discrepancy it has been suggested * that ions are associated with a number of water molecules, and that these complexes, the so-called 'ion-hydrates', migrate as a whole under the influence of the applied *E.M.F.* If the lithium ion is more highly hydrated than sodium, and so on through the series, the size of the ion-hydrate complex may *decrease* in passing down the series from lithium to cæsium; in this way the speeds of the ions would increase with increasing atomic weight. The same argument may be used to explain a similar increase of velocity in passing from fluorine, through the series of halogen ions, to iodine. The hydration decreases, presumably, as the atomic weight of the ion increases.

Although it is generally agreed that there is a larger concentration of water molecules in the vicinity of an ion than in the bulk of the solution, there is no unanimity of opinion concerning the relationship of the water molecules to the ions. In the first place every ion in a given solution may be combined chemically with a definite number of water molecules. Secondly, a dynamic equilibrium may exist between 'bare' ions, water molecules and ion-hydrates of definite composition, viz.



where *n* is an integer. The third possibility is that the electrical

* Bredig, *Z. physikal. Chem.*, 1894, 13, 277 footnote.

field at the surface of an ion attracts water molecules towards it by forces which are electrostatic in nature. These three points of view are not mutually exclusive, and in any given solution there may exist definite hydrates in varying amounts, quite apart from the loose attraction between the hydrated ions and water. The question of the relation between ions and the molecules of solvent is one of great importance and interest; it has reference to non-aqueous, as well as to aqueous solutions, and in the discussion which follows, although more specific reference will be made to the latter, the remarks are applicable to all solutions.

True and Apparent Transport Numbers—If ions are really hydrated and carry water molecules with them during migration, it is clear that transport number measurements will be affected, since the concentration of the solution may be altered. Suppose that each anion and cation has associated with it w_a and w_c , respectively, molecules of water; further, let n_a^T and n_c^T represent the *true* transport numbers, i.e. the fraction of the total current carried by anions and cations respectively. For the passage of one faraday of electricity the cations will carry $w_c n_c^T$ gm. mols. of water in one direction, and the anions will carry $w_a n_a^T$ gm. mols. in the opposite direction. There will thus be a net transfer of

$$w_c n_c^T - w_a n_a^T = x \quad \dots \quad (i)$$

gm. mols. of water from the anode to the cathode compartment. This transfer of water will cause an alteration in the concentration of the solution quite apart from that caused by the migration of ions; in order to determine the true transport number allowance must be made for the water carried by the ions. In the determination of the Hittorf transport number, designated by n_c^H and n_a^H , this correction is not made; hence the values obtained may differ from the true transport numbers. Since n_c^H is the *apparent* number of gm. equivs. leaving the anode compartment, whereas n_c^T is the *true* number, for the passage of one faraday, the difference between the two quantities is equal to the change of concentration resulting from the transfer into the cathode compartment of x gm. mols. of water. If the original solution contained N_s gm. equivs. of salt associated with N_w gm. mols. of water, then the removal of x gm. mols. of water from the anode compartment, for the passage of one faraday, will increase the salt concentration by $(N_s/N_w)x$ gm. equivs. The apparent transport number of the cation will thus appear to be smaller than the true value by this amount, i.e.

$$= n_c^H + \frac{N_s}{N_w} x \quad (ii)$$

In exactly the same way it may be shown that transport of water causes a decrease of concentration in the cathode compartment;

hence the apparent transport number of the anion is greater than the true value, thus

$$n_a^T = n_a^H - \frac{N_{s, \infty}}{N_{w, \infty}} \quad \text{. (iii)}$$

If the net transfer of water (x) could be determined, the true transport numbers could be calculated from the Hittorf values; then by substitution in equation (i), which may be written in the form it

$$w_r = \quad + \frac{n_a^T}{n_c^T} w_{a, \infty} \quad \text{. (iv)}$$

should be possible to determine the relative hydration of the two ions.

Investigations of the Transport of Water—Nernst* suggested that the value of x could be determined by adding to the electrolyte solution an indifferent 'reference' substance, e.g. a sugar, which did not migrate during the passage of the current; as a result of the transfer of water by the ions the concentration of this substance, otherwise remaining constant, should alter. From this change the net transfer of water may be determined and the relative hydration evaluated. The earliest experiments on these lines, however, did not yield any definite results,† but more successful attempts were made by Buchböck‡ and later, with an improved experimental technique, by Washburn.§ The latter considered the best reference substance to be the sugar raffinose, since it did not migrate to any appreciable extent under the influence of an applied *E.M.F.*, and its concentration could be readily determined from its optical rotatory power; recently the use of urea as a reference substance has been proposed.|| In Table VI are given the values obtained by Washburn for the Hittorf transport number (n_c^H), the true transport number (n_c^T), and the net number (x) of gm. mols. of water transferred for the passage of one faraday; the concentration of the electrolyte was approximately 1.25*N* in each case, and the temperature was 25°.

TABLE VI

TRUE AND APPARENT TRANSPORT NUMBERS IN 1.25*N*-SOLUTIONS AT 25°

	HCl.	LiCl.	NaCl.	KCl.	CsCl
n_c^H	0.820	0.278	0.366	0.482	0.485
n_c^T	0.844	0.304	0.383	0.495	0.491
x	0.24	1.5	0.76	0.60	0.53

* See Garrard and Oppermann, *Gött. Nach.*, 1900, 56, 86.

† Garrard and Oppermann, *loc. cit.*; Lobry de Bruyn, *Rec. trav. chim.*, 1903, 22, 430; Morgan and Kanolt, *J. Amer. Chem. Soc.*, 1906, 28, 572.

‡ *Z. physikal. Chem.*, 1906, 55, 563.

§ *J. Amer. Chem. Soc.*, 1909, 31, 322; Washburn and Millard, *ibid.*, 1915, 37, 694; see also Taylor (M.) and Sawyer, *J. Chem. Soc.*, 1929, 2095.

|| Taylor and Sawyer, *loc. cit.*; Taylor *et al.*, *ibid.*, 1932, 2497.

If these values are substituted in equation (iv), it is seen that

$$w_{H^+} = 0.28 + 0.185 w_{Cl^-}$$

$$w_{Li^+} = 4.7 + 2.29 w_{Cl^-}$$

$$w_{Na^+} = 2.0 + 1.61 w_{Cl^-}$$

$$w_{K^+} = 1.3 + 1.02 w_{Cl^-}$$

and

$$w_{Cs^+} = 0.67 + 1.03 w_{Cl^-}$$

Since no actual hydration value of any ion is known, it is impossible to solve these equations, but if the Cl^- ion is assumed to associate with either (a) four, or (b) nine, molecules of water, the results given in Table VII may be calculated.

TABLE VII

POSSIBLE HYDRATION VALUES (ASSUMING 4 OR 9 FOR THE CHLORINE ION)

Cl^-	H^+	Li^+	Na^+	K^+	Cs^+
4	1.0	14	8.4	5.4	4.7
9	2.0	25.3	16.6	10.5	9.9

The results indicate that irrespective of the actual values the order of hydration of the positive ions is: $Li > Na > K > Cs > H$; this is exactly the order required to account for the anomalous transport numbers (p. 45). The highly hydrated lithium ion may thus be larger, and hence move more slowly than the less hydrated caesium ion.

An examination of equations (ii) and (iii) shows that if the electrolyte solution is very dilute, that is N_s/N_w is extremely small, then the true transport number and the Hittorf value will be identical. Riesenfeld and Reinhold* have assumed that this value is the real transport number and is independent of the concentration of electrolyte; any variation of the Hittorf number from this is attributed *entirely* to the transference of water by the ions. Since the term N_s/N_w is a measure of the concentration of the solution it may be represented by c , and equation (ii) written

$$n_c^T = n_c^H + cx \quad \dots \quad (v)$$

If n_c^T is taken as constant for all concentrations, it is found on differentiating that

$$-\frac{dn_c^H}{dc} = x; \quad \dots \quad (vi)$$

hence x may be determined by measuring the slope of the curve connecting the Hittorf transport number with the concentration of the electrolyte; by the use of equation (iv) the relative hydration of the ions may be calculated. It is doubtful, however, if the fundamental assumption of the constancy of the true transport

* *Z. physikal. Chem.*, 1909, 66, 672.

number is justified, even in a simple electrolyte in which complex-ion formation does not occur; it is certain that the velocities of the ions vary with concentration, and if the relative changes for anion and cation are different, the true transport numbers will not be constant.*

Modifications of the Hittorf method enabling true transport and hydration values to be determined have been devised by Remy; † in the first method the anode and cathode compartments were separated by a gelatine gel containing 0.01*N*-potassium chloride, but later parchment membranes were used. The volume change in each electrode compartment was measured when the solution was electrolysed, and allowance made for the amount of water transported by electro-endosmose; the net volume, and hence weight, of water carried from one compartment to the other as a consequence of the passage of one faraday was thus determined. Assuming that the presence of a membrane does not affect the results, the relative hydration of the two ions may be calculated by means of equation (iv); the true and apparent transport numbers are determined from equations (ii) and (iii). The values given in Table VIII have been calculated on the assumption that the chlorine ion carries with it three molecules of water; they appear to be in agreement with those of Washburn.

TABLE VIII

POSSIBLE HYDRATION VALUES (ASSUMING 3 FOR THE CHLORINE ION)

Cl ⁻	H ⁺	Li ⁺	Na ⁺	K ⁺	Cs ⁺	NH ₄ ⁺
3	0.9	12.6	7.4	4.1	3.8	4.4

Baborovský and his collaborators ‡ have used a method similar to that of Remy; the amount of water transported is determined by weighing the anode and cathode compartments, instead of measuring the volume change, and analysing their contents. The hydrations of various ions in *N*-solutions were found to be as follows: H⁺ = 1; Li⁺ = 13-14; Na⁺ = 8-9; K⁺ = 5; Cl⁻ = 4; Br⁻ = 2; and I⁻ = 2. In 0.1*N*-solutions the ionic hydrations appear to be very much greater, e.g. Li⁺ = 62; Na⁺ = 44; Cl⁻ = 26; and Br⁻ = 29. The change resulting from the relatively small dilution is surprising. Both methods involving mem-

* See MacInnes, *J. Amer. Chem. Soc.*, 1921, **43**, 1217.

† *Z. physikal. Chem.*, 1915, **89**, 529; 1925, **118**, 161; 1926, **124**, 394; *Trans. Faraday Soc.*, 1927, **23**, 381; *Fortschritte der Chemie*, 1927, 19.

‡ *Rec. trav. chim.*, 1923, **42**, 229, 553; *Z. physikal. Chem.*, 1927, **129**, 129; **131**, 129; 1933, **163**, 122; *J. Chim. phys.*, 1928, **25**, 452; *Coll. Czech. Chem. Comm.*, 1932, **4**, 200; 1933, **5**, 518.

branes have been criticized on account of the uncertainty of the correction for electro-endosmose.*

Application of Stokes' Law—According to the Stokes' equation concerning the rate of uniform motion of a particle through a viscous medium, $u = f/6\pi r\eta$, where u is the velocity of a particle of radius r , moving through a medium of viscosity η , under the influence of a force f . If two ions have speeds u_1 and u_2 , respectively, when moving under the influence of the same potential gradient, their radii, r_1 and r_2 , will be related by the equation

$$\frac{r_1}{r_2} = \frac{u_2}{u_1} \quad \dots \quad \text{(vii)}$$

When an ion is heavily hydrated the volume of the ion itself will be negligible in comparison with that of its associated water molecules; hence

$$\frac{w_1}{w_2} = \frac{r_1^3}{r_2^3} \quad \text{(viii)}$$

where w_1 and w_2 are the numbers of water molecules carried by the respective ions. It follows, therefore, that

$$\frac{w_1}{w_2} = \left(\frac{u_2}{u_1}\right)^3, \quad \dots \quad \text{(ix)}$$

and so the ratio of the hydration values may be determined. By combining this method with the one described previously (p. 48), Riesenfeld and Reinhold† have obtained the following values for the number of water molecules attached to various ions at infinite dilution: $\text{H}^+ = 0.2$; $\text{OH}^- = 11$; $\text{Li}^+ = 68.158$; $\text{Na}^+ = 59.71$; $\text{K}^+ = 22$; $\text{Ag}^+ = 36$; $\text{ClO}_3^- = 35$; $\text{NO}_3^- = 25.33$; Cl^- , Br^- , $\text{I}^- = 21$; $\text{SO}_4^{--} = 36$. The order for the alkali metals is the same as found by Washburn, but the values are much larger, in some cases so large as to appear unreasonable. In addition to the criticism of the first method already mentioned, the applicability of Stokes' equation to particles of ionic dimensions has been called into question.‡

Remy§ has also made use of equation (vii) to calculate hydration values; he assumed that the hydrogen ion was un-hydrated, and that the specific volume of 1 gm. ion is equal to the value for the gram-atom obtained by Kopp in his work on the molecular volumes of organic compounds.|| From this volume the radius of the hydrogen ion was calculated as 1.09 units, and using the known ionic

* See Taylor and Sawyer, *loc. cit.*, p. 2103.

† *loc. cit.*; see also Ulich, *Z. Elektrochem.*, 1930, 36, 505.

‡ Cf. Sand, *Trans. Faraday Soc.*, 1919, 15, 94; see also Baborovský, *Z. physikal. Chem.*, 1934, 168, 135.

§ *Ibid.*, 1915, 89, 467.

|| *Annalen*, 1855, 96, 172.

velocities (p. 75) the actual radii (R) of various other ions in solution were obtained from equation (vii); this involves the assumption that Stokes' law is applicable to all the ions concerned. The radii (r) of the corresponding atoms have been calculated, in the same units, from the known atomic volumes, and the radius r_w of a water molecule was determined in the same manner. On examining the results Remy found that for many ions $(R - r)/2r_w$ is almost equal to unity; that is, the difference between the actual radius of a hydrated ion and the 'bare' un-hydrated ion is equal to the diameter of a water molecule. This result suggests that each ion is surrounded by a single layer of closely packed water molecules; a very plausible picture of a hydrated ion would be obtained, were it not for the fact that the conclusions are based on values for the radii of un-hydrated ions obtained by a method which is far from satisfactory. In any case the hydrogen ion in solution does not, in all probability, consist of a 'bare' proton (*vide infra*), and even if it did it would not have the same dimensions as a hydrogen atom, as is tacitly assumed in the calculations described. The same objection concerning the difference in size between atoms and ions applies to other elements. Finally it should be mentioned (cf. p. 86) that Stokes' law certainly does not apply to the hydrogen ion, even if it is applicable to others. It is doubtful, therefore, if Remy's picture of hydrated ions is of any significance.

Physical Solvation—Although several different experimental methods indicate that there is an actual transport of water during the passage of an electric current the results do not prove that definite hydrates exist in solution.* Various authors † have adopted the view that instead of definite hydrates there is simply a larger concentration of water molecules in the neighbourhood of an ion, in virtue of the electrical attraction between the charged ion and the water molecule. Water is said to be 'polar', that is it has parts which are positively and negatively charged relative to one another, and in a solution the molecules, or 'dipoles', will orient themselves in a definite manner in relation to an ion. A cation will attract the negative, or oxygen, part of the dipole, whereas an anion will have the positive, or hydrogen, part of the molecule oriented towards it. When the ion attempts to move under the influence of an applied E.M.F. the water molecules tend to be dragged along, and so slow

* See Lindemann, *Trans. Faraday Soc.*, 1919, **15**, 165; *Z. physikal. Chem.*, 1924, **110**, 394; Born, *Z. Elektrochem.*, 1920, **26**, 401. Remy, *Trans. Faraday Soc.*, 1927, **23**, 385 footnote; for review, see Lorenz, *Raumerfüllung und Ionenbeweglichkeit*, 1922.

† Fajans, *Ber. Deut. Physikal. Ges.*, 1919, **21**, 549, 709; Born, *Z. Physik.*, 1920, **1**, 45, 221; Lorenz, *Z. Elektrochem.*, 1920, **26**, 424; *op. cit.*, p. 238; Debye and Hückel, *Physikal. Z.*, 1923, **24**, 305; Schmick, *Z. Physik*, 1924, **24**, 56; see, however, Ashkenasi, *Z. Elektrochem.*, 1922, **28**, 106.

down the motion. According to this concept there is no necessity for a definite attachment of water molecules to the ion, but there may be a continual interchange of 'dipoles' as the ion moves through the solution. The same argument may be applied to the behaviour with other solvents. On the basis of this theory Born* has calculated the 'apparent radius' of a number of ions in solution; in the alkali-metal series the values decrease from lithium to caesium in agreement with the corresponding increase of ionic velocity and transport number. The physical view of solvation would require the sequence of ionic dimensions, and hence of velocities, to be the same in all solvents; although this is true in certain instances it is by no means universally so, as Kraus† has emphasized. It is possible that in addition to the electrostatic solvation which always occurs, the presence in some cases of definite solvate compounds may account for the discrepancies.

The physical theory of solvation, outlined above, permits of the deduction of a simple expression for the energy of solvation of an ion,‡ from which it is possible to determine the electrical contribution to the heat of solvation,§ and this will be the total heat if the solvation is purely electrostatic in origin. The difference between the heats of solvation of the same electrolyte in two solvents can be readily calculated from these expressions, and this should be equal to the heat of transfer of the electrolyte from one solvent to the other; the latter heat quantity may be evaluated from the difference in the integral heats of solution at infinite dilution of the given solute in the two solvents. Experiments with a number of salts in a series of solvents have shown that the agreement between the calculated and observed differences in the heats of hydration is not good,|| and hence it follows that either the Born-Bjerrum equation does not take into account all the physical factors or, what is more probable, the solvation is not exclusively electrostatic in nature.

Review and Discussion—In reviewing the results obtained in investigations of the solvation of ions it may be seen that although the presence of an excess concentration of solute molecules in the vicinity of an ion is accepted, it is not possible to decide on the relationship between the ion and the solvent molecules. It is not improbable that both chemical and physical forces are operative in many instances, whereas physical forces only are operative in others.**

* Born, *Z. Physik*, 1920, 1, 221; see also Webb, *J. Amer. Chem. Soc.*, 1926, 48, 2589.

† *Properties of Electrically Conducting Systems*, 1922, p. 203.

‡ Born, *Z. Physik*, 1920, 1, 45.

§ Bjerrum and Larsson, *Z. physikal. Chem.*, 1927, 127, 369; see also Lange (E.) and Miščenko, *ibid.*, 1930, 149, 1.

|| Gatty, Wolfenden, *et al.*, *J. Chem. Soc.*, 1934, 1368.

** Taylor (M.) *et al.*, *loc. cit.*; Ulich, *Z. physikal. Chem.*, 1934, 168, 141.

For those solutions in which the sequence of the ionic velocities is independent of the nature of the solvent * it is probable that the solvent molecules are held by purely physical forces. In many cases, however,† the order varies with the solvent; for example, the velocity of the chlorine ion in liquid ammonia is greater than that of the iodine ion, but the reverse holds in aqueous solution; in acetone solution the velocities of the lithium, sodium and potassium ions are almost identical, whereas in water the lithium ion is much the slowest. An examination of the results obtained with the lithium and silver ions in liquid ammonia and water may throw some light on the problem; the velocity of the lithium ion is 3.36 times as great in the former solvent as in the latter, but that of the silver ion is only 2.15 times as great in ammonia as in water. It is well known that silver tends to form a complex ion with ammonia in aqueous solution, whereas lithium probably has a strong chemical attachment for water, in view of the hygroscopic nature of lithium salts. In liquid ammonia solution, therefore, the silver ion probably forms a definite solvated complex, with the result that its velocity is not increased in the same proportion as that of the lithium ion which does not form such complexes. In aqueous solution, however, the reverse is probably the case, and hence the ratio of the speed of the silver ion to that of the lithium ion will be greater than in liquid ammonia solution. It may be suggested, therefore, that many ions form definite chemical solvates, but these complexes may attract some further molecules of solvent by purely electrostatic forces.

The existence of a series of isomorphous hydrated sulphates of the general formula $\text{MSO}_4 \cdot 7\text{H}_2\text{O}$, where M may be Mg, Zn, Cd, Co, Ni, Mn, Cr, Fe, suggests the presence of six water molecules co-ordinated with the central atom (or ion), and one molecule of water with the SO_4 ion.‡ The existence of the $[\text{M}(\text{H}_2\text{O})_6]^{++}$ complex in the crystal, and the fact that such crystals invariably separate from solution under normal conditions, suggests that definite ion-hydrates may possibly be present in solution. According to Werner's theory co-ordinated ionic complexes can exist in solution, and in many cases these complexes contain a number of water molecules; such ions are definitely hydrated. It is not

* For such electrolytes the velocity of a given ion is approximately inversely proportional to the viscosity of the medium, see Walden, *Das Leitvermögen der Lösungen*, 1924, Vol. I, p. 369 *et seq.* It should be noted that if the Stokes equation is applicable to an ion the velocity would be expected to be inversely proportional to the viscosity, whether the ion was solvated or not, provided the radius was constant (cf. Lindemann, *Trans. Faraday Soc.*, 1919, 15, 165).

† See Kraus, *op. cit.*, pp. 125-6, 203.

‡ See Sidgwick, *The Electronic Theory of Valency*, 1927, p. 195.

possible to say, however, that in cases of this type all the ions are present as definite solvate compounds; there may be an equilibrium between solvated and un-solvated molecules. In recent years there has been a growing conviction that the 'bare' hydrogen ion does not exist* and that what is generally referred to as the hydrogen ion is really the hydrated ion $\text{H}(\text{H}_2\text{O})^+$, or H_3O^+ ; this is an instance of an ion which is regarded as being always solvated, but as the hydrogen ion is unique the argument may not necessarily extend to other ions. On the whole it may be concluded that many ions form definite chemical compounds,† but there is very little doubt, whether definite solvates are formed or not, the ions also attract molecules of solvent by purely electrostatic forces. The extent of these forces will naturally depend on the tendency of the solvent to form dipoles,‡ and on the intensity of the electrical field at the surface of the ion; this factor will be greater the smaller the size.§ The possibility must also be borne in mind of a gradual transition between electrostatic and chemical solvation, one passing imperceptibly, in certain cases, into the other.||

[In this chapter the subject of solvation has been discussed from the standpoint of ionic velocities and transport numbers; other lines of experiment have been followed, for which reference should be made to the following: Jones (H. C.), *Hydrates in Aqueous Solutions*, 1907; General Discussion, *Trans. Faraday Soc.*, 1907, 3, 123 *et seq.*; Washburn, *Jahrb. Radioakt. Elektronik*, 1908, 5, 493; 1909, 6, 69; *Tech. Quarterly*, 1908, 21, 360; Dhar, *Z. Elektrochem.*, 1914, 20, 57; 1925, 31, 261; Fricke, *ibid.*, 1922, 28, 161; *Z. anorg. Chem.*, 1924, 131, 130; 136, 295; Smith (G. McP.), *J. Amer. Chem. Soc.*, 1915, 37, 722; Kendall *et al.*, *ibid.*, 1917, 39, 2303; Bjerrum, *Z. anorg. Chem.*, 1920, 109, 275; Schreiner, *ibid.*, 1922, 121, 321; 1924, 135, 333; Seith, *Z. physikal. Chem.*, 1925, 117, 257; Glasstone *et al.*, *J. Chem. Soc.*, 1925, 127, 2660; 1926, 2935, 2939; 1927, 635; Sugden, *ibid.*, 1926, 174; Ingham, *ibid.*, 1928, 1917, 2381; 1929, 2059; 1930, 542; Ingold *et al.*, *ibid.*, 1934, 1593; Taylor (H. A.), *J. Physical Chem.*, 1925, 29, 995; Holluta and Werner (H.), *Z. physikal. Chem.*, 1927, 129, 262; Freundlich and Schnell, *ibid.*, 1928, 133, 151; Kosakevitch and Ismailov, *ibid.*, 1930, 150, 295; Ulich, *Z. Elektrochem.*, 1930, 36, 497; Bernal and Fowler, *J. Chem. Physics*, 1933, 1, 515; Bourion, *Compt. rend.*, 1933, 196, 1409; 197, 52; Brintzinger, *Z. anorg. Chem.*, 1935, 222, 113, 312, 317; 223, 101, 106; 1936, 227, 341, 351; Schmitz-Dumont, *ibid.*, 1935, 226, 33; 1936, 227, 347; Sidgwick, *op. cit.*, Chap. XI; Eucken-Wolf, *Hand- und Jahrbuch der Chemischen Physik*, 1933, Vol. 6, Part II, p. 186 (Ulich).]

* See p. 179 *infra*.

† According to Garrick (*Phil. Mag.* 1930, 9, 131; 10, 76, 77; 1931, 11, 741) even co-ordination may be due to physical forces; cf. Magness, *Z. anorg. Chem.*, 1922, 124, 305.

‡ Cf. Walden and Birr, *Z. physikal. Chem.*, 1929, 144, 269.

§ Thomson (J. J.), *Phil. Mag.*, 1914, 27, 755.

|| See Koch, *ibid.*, 1930, 10, 559.

CHAPTER IV

THE CONDUCTANCE OF SOLUTIONS—I

CONDUCTANCE of Electrolytes—The conducting power of a solution is a matter of some importance ; it is evaluated from measurements of the resistance of the electrolyte. The current, I , flowing through a given conductor under the influence of a constant $E.M.F.$, is inversely proportional to the resistance R ; hence $1/R$ is a measure of the conducting power, and is called the **conductance**. Resistances are expressed in ohms, and so conductances are stated in ‘ reciprocal ohms ’, or ‘ mhos ’. The resistance of any conductor varies directly as its length (l cms.), and inversely as its area (a sq. cms.), that is

$$R = \rho \frac{l}{a} \quad (i)$$

where ρ is a constant for the given conductor, called the ‘ specific resistance ’ or ‘ resistivity ’. If a cube of 1 cm. side is considered, $l = 1$, and $a = 1$, and $R = \rho$; therefore, ρ may be defined as the resistance in ohms of a 1 cm. cube of the particular material. The **specific conductance** or **conductivity** * of the conductor is then equal to $1/\rho$ recip. ohms, and is designated by the symbol κ . Hence instead of equation (i), there may be written

$$R = \frac{1}{\kappa} \cdot \frac{l}{a} \quad . \quad . \quad . \quad . \quad . \quad . \quad (ii)$$

If C is the conductance of the solution, then

$$C = \frac{1}{R} = \frac{\kappa a}{l} \text{ recip. ohms.} \quad . \quad . \quad . \quad . \quad (iii)$$

The physical meaning of κ may be seen by considering the application to a conductor of an $E.M.F.$ of 1 volt, i.e. $E = 1$, then by Ohm’s Law, $I = 1/R = C$; for a 1 cm. cube, $a = 1$, $l = 1$, and $C = \kappa$. Hence when a potential difference of 1 volt is applied to a 1 cm. cube of a conductor, the current in amps. flowing is

* The word ‘ conductivity ’ is frequently used in a general sense for conductance, the reciprocal of resistance ; it would seem advisable to restrict its use, however, to the *specific* conductance.

equal to the specific conductance. The definitions given here apply to all conductors, whether metallic or electrolytic.

Solutions—For a given electrolyte the velocities of the anions and cations may, for the present, be considered as constant, and so the quantity of electricity which the solution can carry depends on the number of ions in a given volume; this number depends on the concentration. In order to determine the conducting power of *all* the ions produced by 1 gm. equiv. of electrolyte at different concentrations, it is imagined that two large electrodes are set 1 cm. apart, and between them is placed the *whole* of the solution containing the 1 gm. equiv. The conductance of the resulting system is called the **equivalent conductance** (Λ) at the given concentration. It is a measure of the conducting power of all the ions resulting from the dissociation of 1 gm. equiv. of solute when present in a volume v c.c. of solution: v is called the dilution of the solution, in c.c., and is equal to $1000/c$, where c is the concentration in gm. equiv. per litre. In actual practice the value of the equivalent conductance is calculated from the specific conductance. Since the imaginary electrodes are 1 cm. apart, the volume v c.c. of solution will cover an area of v sq. cms., and as, in general (p. 55),

$$C = \frac{\kappa a}{l},$$

Λ will be equal to C when $a = v$ sq. cms. and $l = 1$; hence it follows that

$$\Lambda = \kappa v = 1000\kappa/c \quad . \quad . \quad . \quad . \quad (\text{iv})$$

The equivalent conductance is thus numerically equal to the specific conductance multiplied by the volume in c.c. containing 1 gm. equiv. of solute. In some work the molecular (or molar) conductance μ is employed; it is defined as the conductance of a solution containing 1 gm. mol. of solute in a volume v_m c.c. of solution, and is equal to κv_m . For uni-univalent electrolytes Λ and μ are, of course, identical.

Experimental Determination of Electrolytic Conductance*—In the earliest attempts made to measure the resistance of a solution the results were so erratic that it was believed Ohm's Law could not be applied to solutions; later, however, when the cause of the uncertain results was discovered, it was concluded that the law was generally accurately obeyed.† During the passage

* For further details and references, consult Davies, *The Conductivity of Solutions*; Wien-Harms, *Handbuch der Experimentalphysik*, XII, Part I, p. 16 (Ebert).

† Accurate studies by Jones (G.) and Bollinger (G. M.), *J. Amer. Chem. Soc.*, 1931, **53**, 1207, have shown that Ohm's Law is applicable to electrolytes

of a current through an electrolytic solution gases are frequently liberated; this not only results in an increase of resistance, but the accumulated gases set up a counter *E.M.F.* (p. 408) opposing the passage of the current. This phenomenon known as 'polarization' is one of the chief sources of error in conductance measurements.*

Elimination of Polarization—An approximate method of eliminating the error due to polarization is to determine the *difference* in resistance of two lengths (l_1 and l_2 cms.) of the same electrolyte using the same electrodes; assuming the polarization effect to be the same in each case, the difference is equal to the resistance of a column of electrolyte $l_1 - l_2$ cms. in length. Polarization could be reduced by using electrodes of the metal present in solution; no gas is then evolved, but the metal dissolves at the anode and is deposited at the cathode. The 'difference' method could then be applied with fair accuracy; it cannot, of course, be used with solutions of acids or alkalis, or of salts of the alkali metals. Another principle is to pass a constant current through the solution and to measure the fall of potential (*E.M.F.*) between two points at a known distance apart; the resistance can then be calculated by Ohm's Law. The method has been recently revived in an improved form,† the fall of potential being measured by the introduction of two subsidiary non-polarizable electrodes; calomel, mercurous sulphate and hydrogen electrodes (pp. 308, 328) have been used for this purpose.

The most satisfactory and most widely applied means for the elimination of polarization is to use a rapidly alternating current of low intensity; as the direction of the current is reversed about a thousand times per second the polarization produced by each pulse of the current is completely neutralized by the next, provided the alternations are symmetrical. This method was first introduced by Kohlrausch ‡ and applied by him and most subsequent workers. The resistance of the solution is generally determined by the use of a Wheatstone's bridge arrangement. In Fig. 6, *C* represents

under normal conditions. The use of very high frequency oscillations of or very high *E.M.F.*'s leads to abnormal results: reference will be made to this subject in Chapter VII.

* By employing high frequency currents the electrodes need not be inserted in the solution; see Denina, *Gazzetta*, 1933, 63, 634; 1934, 64, 675, for special experimental arrangements.

† Newbery, *J. Chem. Soc.*, 1918, 113, 701; Eastman, *J. Amer. Chem. Soc.*, 1920, 42, 1648; Noyes and Marie, *ibid.*, 1921, 43, 1095; Brønsted and Nielsen, *Trans. Faraday Soc.*, 1935, 31, 1478; see also, Cuthbertson and Maas, *J. Amer. Chem. Soc.*, 1930, 52, 494.

‡ Kohlrausch and Nippoldt, *Göt. Nach.*, 1868, 415; *Ann. Physik*, 1869, 138, 280, 370.

the cell containing the electrolyte, R is a variable known resistance, e.g. a resistance box, I is the source of alternating current, T is a current detector, generally a telephone earpiece, and de is a uniform, graduated wire. The resistances in the arms bc , af , and fc are so adjusted that no current can be detected in the instrument T ; the resistances then bear the following ratios :

$$ab/bc = af/fc.$$

If the resistances of the leads to the cell, resistance box and graduated wire are small enough to be neglected,* then it may

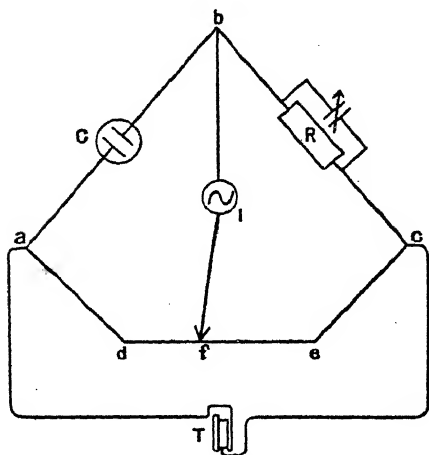


FIG. 6.—Wheatstone's bridge arrangement for the conductance of electrolytes

be said that $C/R = df/fe$, resistances being implied by C and R . The portion de may consist of a length of uniform wire graduated in a thousand parts, or two variable resistance boxes may be used, or two boxes connected by a wire of known resistance for making the final adjustment.† The resistance R should be adjusted to be almost equal to that of C , so that the bridge is balanced when f is almost midway between d and e ; a small error in the final setting will then cause the least discrepancy in the result.

Alternating Current Sources—Kohlrausch introduced the induction coil as a source of alternating current (A.C.) for conductance work; although it is a rather noisy instrument and must be removed from the place of the experiment, it is still a cheap and convenient source of A.C. when high accuracy is not required.‡ For accurate work, however, the induction coil is not satisfactory,§ since it gives an unsymmetrical current with a uni-directional component. It is, therefore, impossible to get complete silence

* In accurate work these resistances must be measured and included.

† Washburn and Bell (J. E.), *J. Amer. Chem. Soc.*, 1913, **35**, 177.

‡ Scheminsky, *Z. physikal. Chem.*, 1923, **104**, 349; 1924, **109**, 435, has described noiseless induction coils designed to work directly from the electric supply mains; the make and break is not performed mechanically, but by means of a neon lamp.

§ Washburn and Bell, *loc. cit.*; Taylor (W. A.) and Acree, *J. Amer. Chem. Soc.*, 1916, **38**, 2396; Washburn, *ibid.*, p. 2431.

in the telephone, and to eliminate polarization. The frequency range of a given induction coil is comparatively small, and it is almost impossible to keep the frequency constant; variations of the note heard in the telephone are thus experienced during the course of an observation. Washburn has used a high-frequency generator, and Taylor and Acree have recommended the Vreeland oscillator* as a source of alternating current; the latter gives a symmetrical sinusoidal current of constant frequency, variable from 160 to 4,200 cycles per second.† These instruments are, however, expensive and recently the thermionic valve has been employed as a source of A.C. for conductance measurements. The application of the valve oscillator for this purpose appears to have been made first by Hall (R. E.) and Adams (L. H.) in 1919,‡ at the suggestion of Miller; the use has been much extended with the increasing availability and cheapness of the valves, and other necessary adjuncts. Various forms of oscillator specially suitable for conductance work have been designed.§

Current Detector—In his earlier work Kohlrausch had used a bifilar galvanometer as an indicator for alternating current, but later || he introduced the telephone receiver as a detector; in 1917 Washburn and Parker (K.),** considered it still to be the most satisfactory instrument for the purpose. It is advisable to 'tune' the telephone so that its fundamental period of vibration coincides with the frequency of the A.C. The best frequency for greatest sensitivity in the ordinary telephone earpiece has been found to be about 1,000 cycles per second. For more accurate determination of the minimum sound in a telephone, especially when solutions of high resistance are being measured, the thermionic valve (low frequency) amplifier has been used in order to increase the sensitivity.††

When high frequency currents are used, with the object of minimizing polarization errors, or for other reasons, the telephone is no longer available as detector: a special arrangement known

* See Vreeland, *Phys. Rev.*, 1908, 27, 286; *Dictionary of Applied Physics*, Vol. II, p. 399.

† See Kraus and Parker (H. C.), *J. Amer. Chem. Soc.*, 1922, 44, 2429.

‡ *Ibid.*, 1919, 41, 1515.

§ Ulich, *Z. physikal. Chem.*, 1925, 115, 377; Burton and Pitt, *Phil. Mag.*, 1928, 5, 939; Woolcock and Murray-Rust, *ibid.*, 1130; Gehman and Weatherby, *ibid.*, 1929, 7, 567; Jones (G.) and Josephs, *J. Amer. Chem. Soc.*, 1928, 50, 1049; Jones (G.) and Bollinger (G. M.), *ibid.*, 1929, 51, 2407; Götte and Schramek, *Z. Elektrochem.*, 1931, 7, 820; Grallert, *ibid.*, 1936, 42, 330; see also, Ebert, *op. cit.*, p. 33.

|| *Ann. Physik*, 1880, 11, 653.

** *J. Amer. Chem. Soc.*, 1917, 39, 235.

†† Hall and Adams, *loc. cit.*; Lorenz and Klauer, *Z. anorg. Chem.*, 1924, 136, 121; Jones and Bollinger, *loc. cit.*; Götte and Schramek, *loc. cit.*

as the 'baretter bridge' has been used in which a D.C. galvanometer acts as the actual detector.*

For general laboratory work an alternating current galvanometer is not to be recommended, but in technical work, where a quiet place is not easily obtainable, the use of such an instrument is inevitable. With a low frequency A.C., e.g. 50 cycles per second, quite good results may be obtained with a galvanometer detector.† Morgan and Hildburgh ‡ have placed an A.C. rectifier in the detector circuit and then made use of a direct current galvanometer in order to indicate the balance point; this method may find application in technical work. The thermal effect of the A.C. has also been used in connection with a sensitive galvanometer, for detection purposes in conductance work.§

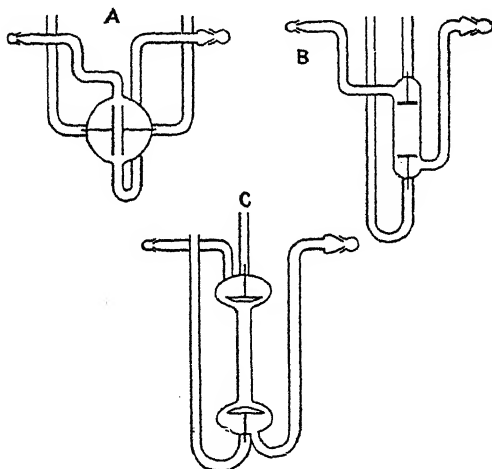


Fig. 7.—Cells for accurate conductance measurements

Conductance Cells—In general the cells used are made of highly insoluble glass or of quartz; they should be very carefully washed and steamed before use. The electrodes are of stout sheet platinum which does not bend readily, and their relative positions are fixed by sealing the electrodes into the sides of the vessel, or

* Schiele and Wien, *Ann. Physik*, 1930, 7, 624; Neese, *ibid.*, 1931, 8, 929.

† Aten, *Chem. Weekblad*, 1921, 18, 51; Aten and Boerlage, *Rec. trav. chim.*, 1929, 48, 698.

‡ *J. Amer. Chem. Soc.*, 1900, 22, 304; see also Glasstone, *Ann. Report Chem. Soc.*, 1933, 30, 295, for references to the use of various A.C. rectifiers, mainly for approximate work.

§ Jander and Pfundt, *Z. anorg. Chem.*, 1926, 153, 219; *Z. Elektrochem.*, 1929, 35, 206.

by joining the glass tubes into which the electrodes are sealed. For the most accurate work the type of cell used depends chiefly on the sensitivity of the telephone detector, and on the conductance of the electrolyte.* Washburn has designed three types of cell, (a) for use with solutions of very small conductance, of the order 10^{-5} to 10^{-7} recip. ohms, Type A, Fig. 7; (b) for solutions of conductance 10^{-3} to 10^{-6} , Type B; and (c) for better conductors, of the order 10^{-4} to 10^{-1} recip. ohms, Type C.

For industrial work 'dipping cells', which can be placed in the liquid to be tested, have been devised; these usually have parallel, vertical electrodes fixed relative to one another. The electrode vessel is open at the bottom, and has holes in the sides to allow free entry of the liquid under examination without air-lock (Fig. 8).

Electrodes—In order to decrease the effect of polarization, even with the use of A.C., Kohlrausch† introduced the use of platinized platinum electrodes; the platinum is coated with a layer of finely divided metal by the electrolysis of a solution containing 3 per cent. of chloroplatinic acid and 0.02–0.03 per cent. of lead acetate.‡ The electrodes must be cleaned thoroughly to remove all traces of electrolyte, and special precautions taken to eliminate chlorine. The finely divided platinum reduces polarization mainly because it has a large surface area, and also because of its catalytic activity in promoting the union between the hydrogen and oxygen liberated by successive pulses of A.C. In some cases the use of platinized platinum is, however, not possible because of the very properties which make it so efficient in the elimination of polarization. The finely divided platinum may catalyse the oxidation of organic compounds, it may cause the decomposition of derivatives of hydrogen peroxide, and it may adsorb electrolyte

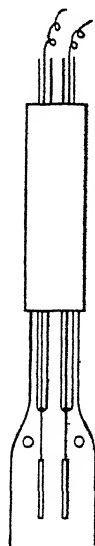


FIG. 8.—Dipping conductance cell

* Washburn, *J. Amer. Chem. Soc.*, 1916, **38**, 2431; Schlesinger and Reed, *ibid.*, 1919, **41**, 1727; Randall and Scott, *ibid.*, 1927, **49**, 636; Smith (F. A.), *ibid.*, p. 2167; Morgan and Lammert, *ibid.*, 1923, **45**, 1692; Jones (G.) and Bollinger (G. M.), *ibid.*, 1931, **53**, 411; Shedlovsky, *ibid.*, 1932, **54**, 1411; Ives and Riley, *J. Chem. Soc.*, 1931, 1998. See also Hartley (H.) and Barrett, *ibid.*, 1913, **103**, 786.

† Kohlrausch and Grottrian, *Ann. Physik*, 1875, **154**, 1, 215.

‡ The lead salt helps the deposition of finely divided platinum, see von Hevesy and Sorniya, *Z. physikal. Chem.*, 1934, **171**, 41; Jones (G.) and Bollinger (D. M.), *J. Amer. Chem. Soc.*, 1935, **57**, 280.

from solution.* It has been suggested that the platinized platinum electrode be heated to redness, when a grey surface is obtained which does not have the harmful effects of the black deposit.† Other workers have used very thin layers of platinum black, but in many cases smooth electrodes were found satisfactory, especially with high frequency A.C. Working with ordinary chloride solutions, which are not liable to oxidation or to be adsorbed, Taylor and Acree ‡ have shown that by using bright platinum electrodes and extrapolating the resistances at various frequencies of A.C. to infinite frequency, the results are almost identical with those given by platinized platinum electrodes. This method is thus available when the platinized electrodes cannot be used.§

Sources of Error—Apart from polarization one of the chief sources of error in conductance measurements is due to the capacity and self-inductance of the circuit; the effect of these is to cause the A.C. in the two arms (*ab* and *bc*, Fig. 6) of the bridge to be out of phase, and no sharp minimum is obtained in the telephone. The actual position of the balance point corresponding to the sound minimum may also be affected. With electrolytes of low conductance it is advisable to balance the capacity of the conductance cell by placing a variable condenser in parallel with the resistance box *R*, Fig. 6; the capacity is adjusted in order to give a sharp minimum in the detector.|| For precision work it is necessary that the apparatus should be adequately shielded and that appropriate parts should be connected to earth.** Capacity and self-inductance may occur in the resistance box, and these are best eliminated by winding the coils in a special way; †† further, all connections should be laid so that wires leading in opposite directions are parallel and close together.

An important source of error in the study of the conductance

* Whetham, *Phil. Trans.*, 1900, 194 A, 321; Tijmstra, *Z. physikal. Chem.*, 1904, 49, 347; Parker (H. C.), *J. Amer. Chem. Soc.*, 1923, 45, 2020; Guerasimov, *J. Russ. Phys. Chem. Soc.*, 1926, 58, 197; Kolthoff, *Rec. trav. chim.*, 1929, 48, 668; de Brouckère, *J. Chim. phys.*, 1928, 25, 294; Walden, *Leitvermögen der Lösungen*, 1924, Vol. I, p. 9 *et seq.*

† Whetham, *loc. cit.*

‡ *J. Amer. Chem. Soc.*, 1916, 38, 2415; see, however, Eastman, *loc. cit.*

§ For other work with smooth electrodes, see Redlich, *Z. physikal. Chem.*, 1928, 136, 331; Kolthoff, *Rec. trav. chim.*, 1929, 48, 668; Kolthoff and Kameda, *J. Amer. Chem. Soc.*, 1931, 53, 821; Shukov, *J. Gen. Chem. Russ.*, 1933, 3, 959.

|| See Sementschenko *et al.*, *Z. physikal. Chem.*, 1933, 167, 188.

** Jones (G.) and Josephs, *loc. cit.*; Shedlovsky, *J. Amer. Chem. Soc.*, 1930, 52, 1793, 1806.

†† See Curtis and Taylor (W. A.), *Physical Rev.*, 1915, 6, 61; Jones and Josephs, *loc. cit.*

of electrolytes lies in the making up and dilution of the solutions ; * various procedures have been suggested to minimize the errors arising in this way and it is recommended that when a series of solutions is being measured the observations should commence with the most concentrated.† Since the conductance of the electrolyte varies appreciably with temperature it is essential to keep the cell in a thermostat ; precautions must, however, be taken to prevent current leakage. The intensity of the A.C. should be kept low, otherwise heating may occur in the experimental solution.‡

Conductance Water—Distilled water is a poor conductor of electricity, but owing to the presence of impurities such as ammonia, carbon dioxide and traces of dissolved substances derived from containing vessels, air and dust, it has a conductance sufficient to affect appreciably the results of accurate work. This source of error is of greatest importance with dilute solutions or weak electrolytes, when the actual conductance is small. If the conductance of the water were simply superimposed on that of the electrolyte the correction would be comparatively simple ; it would only be necessary to prepare distilled water of a known conductance, and subtract this value from that of the solution in order to obtain the conductance due to the added electrolyte. In most cases, however, the impurities in the water can influence the ionization of the electrolyte, or vice versa, or a chemical action may occur, and the conductance of the solution is not the sum of the constituent values. It is therefore desirable to use water which is as free as possible from impurities ; such water is called **conductance water**, or conductivity water. The purest water known was obtained by Kohlrausch and Heydweiller,§ who distilled it repeatedly—forty-two times—under reduced pressure ; this water had a specific conductance of 0.043×10^{-6} recip. ohms at 18° , but only a very small quantity has ever been prepared. Many methods have been proposed for the preparation of conductance water in the labora-

* Berthoud, *Helv. Chim. Acta*, 1930, 13, 17.

† Frazer and Hartley (H.), *Proc. Roy. Soc.*, 1925, 109 A, 351 ; Randall and Scott, *loc. cit.* ; Martin, *J. Chem. Soc.*, 1928, 3270 ; Shedlovsky and Brown (A. S.), *J. Amer. Chem. Soc.*, 1934, 56, 1066.

‡ For a discussion of precision measurements, reference may also be made to the following : Kraus and Parker (H. C.), *J. Amer. Chem. Soc.*, 1922, 44, 2422, 2429 ; Parker (H. C.), *ibid.*, 1923, 45, 1366, 2020 ; Parker (H. C.) and Parker (E. W.), *ibid.*, 1924, 46, 312 ; Morgan and Lammert, *ibid.*, 1923, 45, 1692 ; 1924, 46, 1117 ; 1926, 48, 1220 ; Randall *et al.*, *ibid.*, 1924, 46, 2418 ; 1927, 49, 636, 1486 ; Jones (G.) *et al.*, *ibid.*, 1928, 50, 1049 ; 1929, 51, 2407 ; 1931, 53, 411, 1207 ; 1933, 55, 1780 ; 1935, 57, 272, 280 ; Shedlovsky, *ibid.*, 1930, 52, 1793, 1801 ; 1932, 54, 1411 ; Ebert, *op. cit.*

§ *Ann. Physik*, 1894, 53, 209 ; *Z. physikal. Chem.*, 1894, 14, 317.

tory,* and a number of special stills are available as commercial products. For most purposes conductance water may be obtained by distilling good distilled water, to which a little permanganate or Nessler's solution is added. A Jena-glass retort is used, and the vapour is condensed either in a block-tin condenser, or in a Jena-glass tube fitted inside a Liebig's condenser; all corks must be covered with tin-foil. The water so obtained has a specific conductance of approximately 1×10^{-6} recip. ohms at 18° . It has been claimed that if only part of the water vapour is condensed and the remainder allowed to carry off gaseous impurities, 'ultra-pure' water with a conductivity of 0.05×10^{-6} mhos at 18° can be obtained on a fairly large scale.† Water of such purity, however, is only desirable in the most accurate work and provided air can be rigidly excluded; on exposure to air water dissolves carbon dioxide, and its specific conductance rises to about 0.8×10^{-6} mhos at 18° . This is called 'equilibrium water' and is quite satisfactory for most conductance work.

The Water Correction—The extent of the water correction depends on the nature of the electrolyte; although there is no general agreement concerning these corrections,‡ the following conclusions would probably be accepted. Working with equilibrium water the impurity is mainly carbon dioxide, and the conductance due mainly to ionized carbonic acid. If the electrolyte is a strong acid of concentration greater than $10^{-4}N$, the ionization of the weak acid is depressed § to such an extent that its contribution towards the total conductance may be neglected. In these circumstances no water correction is necessary; at most the value for 'ultra-pure' water, i.e. 0.05×10^{-6} mhos, may be subtracted from the total. If the concentration of strong acid is less than $10^{-4}N$, a small correction is necessary; the value of this may be calculated from the known 'ionization constant' (p. 103) of carbonic acid.|| With a solution of a weak acid the correction is again negligible if the specific conductance of the solution is greater than

* Kendall, *J. Amer. Chem. Soc.*, 1916, 38, 2460; Bencowitz and Hotchkiss, *J. Physical Chem.*, 1925, 29, 705; Bengough *et al.*, *J. Chem. Soc.*, 1927, 2156; Stuart and Wormwell, *ibid.*, 1930, 85; Vogel (A. I.), *ibid.*, 1931, 1201; Taylor, *Physical Chemistry*, 1931, p. 647 (Partington), for summary.

† Kraus and Dexter, *J. Amer. Chem. Soc.*, 1922, 44, 2468; Bencowitz and Hotchkiss, *loc. cit.*; see also Gostkovski, *Z. physikal. Chem.*, 1934, 170, 149.

‡ For reviews and discussion, see Kendall, *J. Amer. Chem. Soc.*, 1916, 38, 1480, 2460; 1917, 39, 7; Washburn, *ibid.*, 1918, 40, 109; Kolthoff, *Rec. trav. chim.*, 1929, 48, 664; Davies, *Trans. Faraday Soc.*, 1929, 25, 129; *The Conductivity of Solutions*, 1933, Chap. IV; Taylor (T. I.), *J. Physical Chem.*, 1933, 37, 765.

§ *Vide infra*, p. 102.

|| See Kolthoff, *loc. cit.*

2×10^{-5} mhos; if less than this value the appropriate correction may be calculated by the method of Walker and Cormack.*

The correction to be applied when working with solutions of bases is very uncertain; if anything a correction should be *added* to the measured conductance, since the partial neutralization which occurs when carbon dioxide is added to an alkaline solution results in a *decrease* of conductance. Probably 'ultra-pure' water should be used if accurate results are desired, although a method of calculating the corrections has been suggested.† When working with neutral salts the ionization, and conducting power, of carbonic acid is not greatly affected; hence the whole conductance of the 'equilibrium' water should be subtracted from that of the solution. For salts of weak bases and strong acids the correction is probably less than this amount; for solutions of salts of strong bases and weak acids, which are alkaline (p. 190), the correction has been uncertain, but methods have been described for calculating its amount both in 'equilibrium water', assuming the conductance of the latter to be due to carbonic acid, and in water to which a small excess of barium hydroxide, to precipitate the carbonic acid as barium carbonate, has been added.‡ With non-aqueous solvents of the hydroxylic type, e.g. alcohols, the corrections are probably similar to those for water; other solvents must be considered on their own merits.§ In general the solvent should be as pure as possible, so that the correction is, in any case, small.

The Cell Constant—The specific conductance (κ) is connected with the resistance (R) of the solution by the relation (see p. 55., equation ii)

$$\kappa = \frac{l}{aR} \quad \dots \dots \dots (v)$$

where l may be regarded as the distance apart of two similar electrodes, and a the area of cross-section of each. For a given cell, at a definite temperature, with fixed electrodes l/a is a constant, called the **Cell Constant**. This quantity may be obtained by direct measurement of l and a , but this is very rarely done, since it is possible to determine the value of the cell constant by measuring the resistance of a solution of known specific conductance. The electrolyte almost invariably chosen for this purpose is potassium

* *J. Chem. Soc.*, 1900, 77, 5; *vide infra*, p. 103.

† Kolthoff, *loc. cit.*

‡ Davies, *Trans. Faraday Soc.*, 1932, 28, 607; Ives, *J. Chem. Soc.*, 1933, 313, 561; Jeffery, Vogel (A. I.) and Lowry (H. V.), *ibid.*, 1933, 1637; 1934, 166; 1935, 21; see also p. 200 *infra*. For an approximate method of correction, see Dippy *et al.*, *ibid.*, 1934, 1888; 1935, 343.

§ See Wynne-Jones, *J. Physical Chem.*, 1927, 31, 1647; also, Jones (G. E. M.) and Hughes (O. L.), *J. Chem. Soc.*, 1934, 1197.

chloride solution,* and until recently the accepted values for the specific conductance at various dilutions were those obtained by Kohlrausch and his collaborators.† It was suggested at one time ‡ that the results of Kohlrausch were about 0.15 per cent. too high, but the very careful work of Jones (G.) and Bradshaw § has shown that they were surprisingly accurate. The latest values for the specific conductances of potassium chloride solutions containing 1.0, 0.1 and 0.01 gm. equiv. (1 gm. equiv. = 74.553 gms.) in one cubic decimetre (i.e. 0.999973 litres) are given in Table IX; the solutions are designated by 1.0 *D*, 0.1 *D* and 0.01 *D* respectively, and contain 76.627, 7.4789 and 0.74625 gm. of potassium chloride to 1,000 gms. of water. These values may be regarded as standards from which cell constants can be calculated.

TABLE IX
SPECIFIC CONDUCTANCES OF 1.0 *D*, 0.1 *D* AND 0.01 *D* SOLUTIONS OF POTASSIUM CHLORIDE

Temp.	1.0 <i>D</i> .	0.1 <i>D</i> .	0.01 <i>D</i> .
0° .	0.065176	0.0071379	0.00077364
18° .	0.097838	0.0111667	0.00122052
25° .	0.111342	0.0128560	0.00140877

When the constant of a given cell has been determined it may be used for the measurement of the specific conductance of any solution.‖ If *R* is the resistance of the solution when placed in the given cell, then

$$\kappa = \frac{\text{Cell constant}}{R} \quad \text{. (vi)}$$

Multiplying the value of κ so obtained by *v*, the volume of solution in c.c. containing one gm. equiv. of electrolyte, gives the equivalent conductance of the given electrolyte.**

Results of Conductance Measurements—Numerous measurements, of varying accuracy, have been made of the conductances of salts, acids and bases in aqueous and non-aqueous solutions. As the latter solutions show certain abnormalities they will be discussed separately, and aqueous solutions only will be dealt with in this section. A full compilation of results of conductance measure-

* Johnson and Hulett, *J. Amer. Chem. Soc.*, 1935, 57, 256, suggest that saturated solutions of sparingly soluble salts might be used.

† See Kohlrausch and Holborn, *Leitvermögen der Elektrolyte*, 1916, p. 76.

‡ Parker (H. C.) and Parker (E. W.), *J. Amer. Chem. Soc.*, 1924, 46, 312.

§ *Ibid.*, 1933, 55, 1780.

‖ For procedure when studying dilute solutions, see Frazer and Hartley (H.), *loc. cit.*

** Wark, *J. Physical Chem.*, 1930, 34, 885, suggests that the cell constant should be determined at various bridge readings.

ments, with references, will be found in International Critical Tables, Vol. VI, page 231 *et seq.* The values given in Table X are mainly taken from this compilation; a few typical electrolytes have been chosen in order to illustrate general tendencies.

TABLE X
EQUIVALENT CONDUCTANCES AT 18° FOR VARIOUS DILUTIONS (LITRES)
IN RECIPROCAL OHMS

	1.	2.	5.	10.	20.	100.	500.	1,000.	2,000.	∞
HCl . .	300.5	326.6	341.5	350.1	357.6	369.3	375.5	377	—	380.4
NaCl . .	74.2	80.8	87.5	91.8	95.5	101.7	105.3	106.3	106.9	109.0
KOH . .	184	197	207	213	218	228	233	234	—	238.0
$\frac{1}{2}$ BaCl ₂ .	70.0	77.2	85.2	90.6	95.9	106.5	113.6	115.4	116.8	120.9
$\frac{1}{2}$ CdCl ₂ .	21.6	29.6	41.0	50.0	60.1	82.9	99.5	104.8	—	111.9
$\frac{1}{2}$ CuSO ₄ .	25.7	30.7	37.6	43.8	51.1	71.6	91.8	98.4	103.4	114.4
$\frac{1}{2}$ K ₂ SO ₄ .	71.5	78.3	87.8	94.8	101.8	115.6	124.4	126.7	128.3	132.8
C ₂ H ₃ O ₂ .	1.32	2.01	3.24	4.60	6.48	14.3	30.2	41	57	350
NH ₄ OH .	0.89	1.35	2.30	3.3	4.6	9.6	20.6	28	38	238

The results indicate quite clearly that the equivalent conductance, and hence the conducting power of the ions in 1 gm. equiv. of electrolyte, increases with dilution until it approaches a constant value in very dilute solutions. According to the theory of electrolytic dissociation, as originally proposed by Arrhenius, this increase was attributed to increased dissociation of the electrolyte into its constituent ions as the solution was diluted. At very high dilutions the ionization must be almost complete; hence the equivalent conductance approaches a limiting value. Now, however, this explanation is only considered satisfactory for weak electrolytes, e.g. organic acids and bases; according to modern views (p. 134) strong electrolytes, e.g. strong acids, bases and most salts, may be regarded as almost completely ionized at all concentrations, and the change of equivalent conductance cannot be attributed to a varying degree of ionization. Owing to the mutual electrical interaction of ions, and of ions and water molecules, it is believed that the speed of an ion is reduced as the concentration of the solution is increased; hence the conducting power, i.e. the equivalent conductance, of a solution of a strong electrolyte decreases with increasing concentration, although the degree of ionization may alter only slightly. For an intermediate electrolyte, e.g. copper sulphate, it is probable that both the degree of ionization and the ionic speeds change appreciably with concentration.

Equivalent Conductance at Infinite Dilution.—In any case the limiting value of the equivalent conductance at 'infinite dilution', represented by Λ_0 ,* is a measure of the conducting power

* The practice of using Λ_0 to represent the conductance at infinite dilution is becoming less common.

of 1 gm. equiv. of an electrolyte when it is completely ionized and the ions do not influence one another. In some cases Λ_0 may be obtained by simple extrapolation to zero of the curve of Λ against the concentration of the solution, but more accurate results have been obtained with strong electrolytes by the use of empirical formulæ, such as

$$\Lambda = \Lambda_0 - ac^{1/3} \quad \text{. (vii)}$$

or

$$\Lambda = \Lambda_0 - bc^{1/2} \quad \text{. (viii) }^*$$

where c is the concentration of the solution when the equivalent conductance is Λ , and a and b are constants. To use these equations Λ at various concentrations is plotted against $\sqrt[3]{c}$ or \sqrt{c} , and the resulting curve, which should be a straight line, is extrapolated to $c = 0$; the value of Λ so obtained is the equivalent conductance at infinite dilution. An alternative equation

$$\Lambda = \Lambda_0 - Bc^{0.45} \quad \text{. (ix)}$$

has been stated \dagger to be in good agreement with experimental results, and other forms of the square-root equation have been proposed. \ddagger An analysis of a large number of conductance measurements led Ferguson and Vogel \S to propose the general formula for extrapolation :

$$\Lambda = \Lambda_0 - Bc^n, \quad \text{. (x)}$$

where n depends on the nature of the electrolyte, and generally varies between 0.4 and 0.55 (see p. 161). All the methods of extrapolation naturally give results which are close together, since they are based on the same measurements of Λ in dilute solutions, but they are not identical. In Table XI is given a selection of the values of Λ_0 at 18° obtained by the use of (a) Kohlrausch's cube-root formula, (b) Davies' square-root equation, and (c) Ferguson and Vogel's general method.

TABLE XI
EQUIVALENT CONDUCTANCES AT INFINITE DILUTION DETERMINED BY THE
USE OF DIFFERENT EXTRAPOLATION FORMULÆ (18°)

	Kohlrausch.	Davies.	Ferguson and Vogel.
Potassium chloride . .	130.1	129.92	130.04
Sodium chloride . . .	109.0	108.76	109.02
Lithium chloride . . .	98.9	98.69	99.07

* Kohlrausch, *Ann. Physik*, 1885, 26, 161; 1893, 50, 385; *Z. Elektrochem.*, 1907, 13, 333. The square root equation has a theoretical basis (Chapter VII).

\dagger Lorenz, *Z. anorg. Chem.*, 1919, 108, 191; Walden, *ibid.*, 1921, 115, 49, 81.

\ddagger Davies, *J. Physical Chem.*, 1925, 29, 473; Lattey, *Phil. Mag.*, 1927, 4, 831.

\S *Ibid.*, 1925, 50, 971; *Trans. Faraday Soc.*, 1927, 25, 404

The empirical procedures already described are likely to be replaced by one having a theoretical basis ; * the method is applicable to strong electrolytes which, according to modern theories may be regarded as completely ionized at all reasonable concentrations. It will be seen later (Chapter VII) that Debye, Hückel and Onsager have deduced the equation

$$\Lambda_0 = \Lambda + (A + B\Lambda_0)\sqrt{c}, \quad . \quad . \quad . \quad (xi)$$

where A and B are constants which may be calculated theoretically ; for an aqueous solution of a uni-univalent electrolyte the values are 50.3 and 0.225 at 18°, and 59.79 and 0.2274 at 25°, respectively. If the Onsager equation is applicable to an electrolyte it is obviously a simple matter to determine Λ_0 from the measured equivalent conductances at various concentrations. In actual practice the Λ_0 values are not the same for all concentrations, because of departure from ideal behaviour, but if these are plotted against c a straight line is obtained, which may be extrapolated to $c = 0$ to give the correct equivalent conductance at infinite dilution. Working in this manner Shedlovsky obtained 129.4, 108.5 and 98.4 recip. ohms for potassium, sodium and lithium chlorides, respectively, at 18° ; these results are lower than any of those quoted in Table XI although apparently based on the same data.

The extrapolation formulæ described here are not applicable to solutions of weak and intermediate electrolytes ; since the degree of dissociation is generally small, measurements would have to be made in extremely dilute solutions to be of any value for extrapolation purposes. In order to determine the value of Λ_0 for such solutions other methods, to be described later (see pp. 73, 165), must be used.†

* Shedlovsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1405.

† For references to other methods of extrapolation see Taylor, *Physical Chemistry*, 1931, p. 652 *et seq.* (Partington) ; Davies, *op. cit.*, Chapter VI ; Randall and Scalione, *J. Amer. Chem. Soc.*, 1927, **49**, 1486.

CHAPTER V

THE CONDUCTANCE OF SOLUTIONS—II

THE Independent Migration of Ions—If the equivalent conductances at infinite dilution of some pairs of salts having an ion in common are examined, certain regularities will be observed. Consider the following examples :

Λ_0 at 18° for KCl = 130.0,	NaCl = 108.9 ;	Difference = 21.1
KNO ₃ = 126.3,	NaNO ₃ = 105.2 ;	„ = 21.1
$\frac{1}{2}$ K ₂ SO ₄ = 133.0,	$\frac{1}{2}$ Na ₂ SO ₄ = 111.9 ;	„ = 21.1
Λ_0 at 18° for KCl = 130.0,	$\frac{1}{2}$ K ₂ SO ₄ = 133.0 ;	Difference = 3.0
NaCl = 108.9,	$\frac{1}{2}$ Na ₂ SO ₄ = 111.9 ;	„ = 3.0

The difference between equivalent conductances at infinite dilution of the sodium and potassium salts of the same anion is seen to be constant, independent of the nature of the anion. The differences between the conductances of chlorides and sulphates of a given cation are similarly independent of the latter. This relation was discovered by Kohlrausch * and was found to apply generally for any pairs of cations or anions. It appears, therefore, that every ion at infinite dilution contributes a definite amount towards the equivalent conductance, irrespective of the nature of the other ion with which it is associated in the electrolyte. The value of Λ_0 may then be regarded as the sum of two independent factors, one for each ion. These factors are called the **Ion Conductances**, or the **Mobilities of the Ions**, since they are proportional to the velocities of the ions (see p. 75) ; they may be represented by the symbols Λ_c and Λ_a for 1 gm. equiv. of cation and anion, respectively. The discovery of Kohlrausch is usually called the **Law of Independent Migration of Ions**, and it can be expressed in the form

$$\Lambda_0 = \Lambda_c + \Lambda_a \quad \dots \dots \dots (i)$$

The values of the ionic mobilities at infinite dilution are definite constants for each ion, depending only on the temperature.

It has been shown that at infinite dilution all the ions that can be derived from the electrolyte are taking part in conducting the current ; hence solutions each containing 1 gm. equiv. of different electrolytes will contain, under these conditions, equivalent num-

* *Gött. Nach.*, 1876, 213 ; *Ann. Physik*, 1879, 6, 1.

bers of ions. The total ionic charge will then be the same, and the difference in the equivalent conductances can only be attributed to the different speeds of the ions of the electrolytes. The equivalent conductance at infinite dilution must, therefore, be proportional to the sum of the speeds of the two constituent ions, thus

$$\Lambda_0 = k(u + v) = ku + kv, \quad \dots \quad (\text{ii})$$

where k is a constant for *all* electrolytes. In this equation ku represents the contribution of the cation, and kv that of the anion; each ion, at infinite dilution, moves quite independently of the nature or speed of the other. It follows, therefore, on comparing equations (i) and (ii), that

$$\Lambda_c = ku, \text{ and } \Lambda_a = kv, \quad \dots \quad (\text{iii})$$

and so the name 'mobility' is justified.

Further, $u + v = n_c$ the transport number of the cation,

$$\dots \dots \dots \frac{\Lambda_c}{\Lambda_a + \Lambda_c} = \frac{\Lambda_c}{\Lambda_0} \quad (\text{iv})$$

$$\therefore \Lambda_c = n_c \Lambda_0, \text{ and similarly } \Lambda_a = n_a \Lambda_0 \quad \dots \quad (\text{v})$$

By means of these equations the mobilities of the ions may be calculated from a knowledge of equivalent conductances and the transport numbers; the latter should, if possible, be the values extrapolated to infinite dilution.* For example, at 18° , Λ_0 for potassium chloride is 130.0 recip. ohms; the transport numbers of cation and anion in a dilute solution are 0.496 and 0.504 respectively, hence

$$\Lambda_{K^+} = 0.496 \times 130.0 = 64.5 \text{ recip. ohms}$$

$$\text{and } \Lambda_{Cl^-} = 0.504 \times 130.0 = 65.5 \quad ,, \quad ,,$$

For sodium chloride at 18° , $\Lambda_0 = 108.9$, n_c and n_a are 0.398 and 0.602 respectively, therefore $\Lambda_{Na^+} = 43.4$, and $\Lambda_{Cl^-} = 65.5$ recip. ohms. From a knowledge of the ionic mobility of one constituent of an electrolyte the value for the other may be calculated, e.g. Λ_0 for $\frac{1}{2}K_2SO_4$ is 133.0, but Λ_{K^+} is known from measurements on potassium chloride as 64.5 recip. ohms,

$$\therefore \Lambda_{\frac{1}{2}SO_4^{--}} = \Lambda_0 - \Lambda_{K^+} = 133.0 - 64.5 = 68.5 \text{ recip. ohms.}$$

It should be noted that the ionic mobilities, or conductances, are expressed in terms of 1 gm. equiv.; hence the use of Λ_0 for $\frac{1}{2}K_2SO_4$. Proceeding in this manner the mobilities of a large number of ions have been determined; the values for a given ion obtained from a consideration of different salts are not always identical, although

* Cf. MacInnes, Shedlovsky and Longsworth, *J. Amer. Chem. Soc.*, 1932, 54, 2758, who extrapolate the ion conductances.

they should be theoretically, but are so close together that an average is justifiable. A number of accepted values, taken mainly from International Critical Tables, Vol. VI, page 230, together with the temperature coefficients are given here (Table XII).*

TABLE XII
IONIC MOBILITIES, OR CONDUCTANCES, AT INFINITE DILUTION
TEMPERATURE 18°

Ion.	c	Ion.	Λ	c
H ⁺ .	315.2	OH ⁻ .	173.8	0.018
Cs ⁺ .	67.46	$\frac{1}{2}$ CrO ₄ ²⁻	72	—
Tl ⁺ .	65.3	$\frac{1}{2}$ SO ₄ ²⁻	68.5	0.0227
K ⁺ .	64.20	Br ⁻ .	67.31	0.0215
NH ₄ ⁺ .	64.3	I ⁻ .	66.25	0.0213
$\frac{1}{2}$ Pb ²⁺ .	61	Cl ⁻ .	65.24	0.0216
$\frac{1}{2}$ Ba ²⁺ .	55	ClO ₄ ⁻ .	64	—
Ag ⁺ .	53.8	$\frac{1}{2}$ C ₂ O ₄ ²⁻	63.0	0.0231
$\frac{1}{2}$ Ca ²⁺ .	51	NO ₃ ⁻ .	61.62	0.0205
$\frac{1}{2}$ Sr ²⁺ .	51	$\frac{1}{2}$ CO ₃ ²⁻	60	—
$\frac{1}{2}$ Zn ²⁺ .	47.0	SCN ⁻ .	56.7	0.0221
$\frac{1}{2}$ Cd ²⁺ .	46.4	ClO ₃ ⁻ .	54.87	0.0215
$\frac{1}{2}$ Cu ²⁺ .	45.9	IO ₄ ⁻ .	48	—
$\frac{1}{2}$ Mn ²⁺ .	44	BrO ₃ ⁻ .	47.6	—
$\frac{1}{2}$ Co ²⁺ .	43	F ⁻ .	46.6	0.0238
Na ⁺ .	43.16	CHO ₂ ⁻ .	46	—
$\frac{1}{3}$ Al ³⁺ .	40	C ₂ H ₃ O ₂ ⁻ .	35	0.0238
Li ⁺ .	33.02	IO ₃ ⁻ .	33.78	0.0214
$\frac{1}{2}$ Be ²⁺ .	28	C ₂ H ₅ O ₂ ⁻ .	31	—

The variation of ionic conductance with temperature may be represented by the equation

$$\Lambda_t = \Lambda_{18} [1 + c(t - 18)],$$

where Λ_t is the ionic conductance at t° , and Λ_{18} at 18° C. The quantity c , which is equal to $\frac{1}{\Lambda_{18}} \cdot \frac{d\Lambda}{dt}$, is called the 'temperature coefficient'; some of the values of this quantity are given in Table XII.† It will be seen that the temperature coefficients are smallest for the ions with the largest velocity, but for most ions the values lie between 0.022 and 0.025. The general effect of the small temperature coefficient for ions of high velocity is to tend to equalize the values for all ions as the temperature increases; as

* See also Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, 34, 454; Walden and Ulich, *Z. physikal. Chem.*, 1923, 106, 49; Hölzl, *Monatsh.*, 1930, 55, 132; 56, 79; Jeffery and Vogel (A. I.), *J. Chem. Soc.*, 1931, 1715; 1932, 400; *Phil. Mag.*, 1934, 17, 582; MacInnes, Shedlovsky and Longworth, *loc. cit.*; Lasselle and Aston, *J. Amer. Chem. Soc.*, 1933, 55, 3067.

† See Kohlrausch, *Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 1026; 1902, 572; *Proc. Roy. Soc.*, 1903, 71 A, 338.

has already been seen (p. 38), this has the effect of causing transport numbers to approach 0.5 as the temperature is raised. Attempts have been made to obtain equations connecting the temperature coefficient with the ionic mobility, but as no theoretical interpretation of these equations has been possible they are of little fundamental value.*

Although the ionic conductances of the alkali metals increase with increasing atomic weight, probably on account of hydration effects (p. 45), the conductances of complex ions or of organic ions generally decrease as the number of atoms in the complex increases. Bredig † has made a very full compilation of ionic conductances, and the results quoted in Table XIII are mostly taken from his work.

TABLE XIII
EQUIVALENT CONDUCTANCES OF COMPLEX AND ORGANIC IONS (25°)

Ion.		No. of atoms. Λ_0		Ion.		No. of atoms. Λ_0	
$\text{Co}(\text{NH}_3)_4(\text{CO}_3)^+$	21	35	NH_4^+	5	70.4
$\text{Co}(\text{NH}_3)_5(\text{NO}_2)^{++}$	24	23.5	$\text{NH}_3(\text{CH}_3)^+$	8	57.6
$\text{Co}(\text{NH}_3)_6^{+++}$	25	25.7	$\text{NH}_2(\text{CH}_3)_2^+$	11	50
$\text{H}\cdot\text{COO}^-$	4	51.2	$\text{NH}(\text{CH}_3)_3^+$	14	47
$\text{CH}_3\cdot\text{COO}^-$	7	38.3	$\text{N}(\text{CH}_3)_4^+$	17	43.6
$\text{C}_2\text{H}_5\cdot\text{COO}^-$	10	34.3	$\text{N}(\text{C}_2\text{H}_5)_4^+$	29	32.2
$\text{C}_3\text{H}_7\cdot\text{COO}^-$	13	30.8	$\text{N}(\text{C}_2\text{H}_5)_3(\text{C}_3\text{H}_7)^+$	32	29.5
$\text{C}_5\text{H}_{11}\cdot\text{COO}^-$	19	27.4	$\text{N}(\text{C}_2\text{H}_5)_2(\text{C}_4\text{H}_9)^+$	35	29.1
$\text{C}_6\text{H}_5\cdot\text{COO}^-$	14	31.2	$\text{N}(\text{C}_3\text{H}_7)_4^+$	41	23

Applications of Ion Conductances—The values of ion conductances at infinite dilution are useful for calculating the equivalent conductances of weak electrolytes, e.g. acetic acid and ammonium hydroxide; these are so slightly ionized even in the most dilute solutions of which it is possible to determine the conductance, that extrapolation to infinite dilution is not accurate. The value of Λ_0 for acetic acid, however, is the sum of the ion conductances for the hydrogen and acetate ions; the former can be determined from measurements on a strong acid, and the latter from observations on sodium acetate, which being a salt is strongly ionized. Therefore

$$\Lambda_0 \text{ for } \text{CH}_3\cdot\text{COOH} = \Lambda_{\text{H}^+} + \Lambda_{\text{CH}_3\cdot\text{COO}^-} \\ = 315.2 + 35.0 = 350.2 \text{ recip. ohms at } 18^\circ.$$

Similarly

$$\Lambda_0 \text{ for } \text{NH}_4\text{OH} = \Lambda_{\text{NH}_4^+} + \Lambda_{\text{OH}^-} \\ = 64.3 + 173.8 = 238.1 \text{ recip. ohms at } 18^\circ.$$

* Kohlrausch, *loc. cit.*; Nernst, *Theoretical Chemistry*, Eng. trans., 1923, p. 429; see, however, Fuoss, *J. Amer. Chem. Soc.*, 1934, 56, 1855; Angel, *Z. physikal. Chem.*, 1934, 170, 81.

† *Ibid.*, 1894, 13, 191.

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As a corollary to the law of independent migration of ions it follows that

$$\Lambda_0 \text{ for } \text{CH}_3\cdot\text{COOH} = \Lambda_{\text{HCl}} + \Lambda_{\text{CH}_3\cdot\text{COONa}} - \Lambda_{\text{NaCl}}.$$

This type of formula may be used instead of calculating the separate ion conductances.

The method is also of value in connection with sparingly soluble salts, since in these circumstances a series of measurements at known concentrations is extremely difficult. Thus for lead sulphate and silver chloride,

$$\begin{aligned} \Lambda_0 \text{ for } \frac{1}{2}\text{PbSO}_4 &= \Lambda_{\frac{1}{2}\text{Pb}^{2+}} + \Lambda_{\frac{1}{2}\text{SO}_4^{2-}} \\ &= 61 + 68 = 129 \text{ recip. ohms at } 18^\circ; \end{aligned}$$

$$\begin{aligned} \Lambda_0 \text{ for } \text{AgCl} &= \Lambda_{\text{Ag}^+} + \Lambda_{\text{Cl}^-} \\ &= 53.8 + 65.2 = 119.0 \text{ recip. ohms at } 18^\circ. \end{aligned}$$

Absolute Velocities of Ions—The ion conductances have been shown to be directly proportional to the velocities of the ions; the proportionality constant can be determined, and so the absolute velocities of the ions may be calculated from a knowledge of the conductances. Consider a very dilute solution of an electrolyte containing c gm. equiv. of solute per litre: it will therefore contain $c/1000$ gm. equiv. per c.c. Imagine this quantity of solution placed in a cube of 1 cm. side with electrodes of 1 cm. squares at opposite faces, and suppose that a difference of potential of 1 volt is then applied between these two electrodes. Since the solution is very dilute the solute may be supposed to be completely dissociated into ions; the equivalent conductance may then be regarded as equal to that at infinite dilution. If κ is the actual conductance of the 1 cm. cube, it is also the specific conductance of the solution. Since by equation (iv)

$$\Lambda = 1000\kappa/c$$

and

$$\Lambda = \Lambda_c + \Lambda_a$$

it follows that

$$\kappa = c(\Lambda_c + \Lambda_a)/1000 \quad \dots \dots \dots \text{(vi)}$$

By Ohm's Law the current flowing is equal to the fall of potential (E) multiplied by the conductance; in the present case $E = 1$ volt, and the conductance is κ recip. ohms, hence the current flowing is κ amps., i.e. $c(\Lambda_c + \Lambda_a)/1000$ amps. During every second, therefore, the quantity of electricity flowing through the 1 cm. cube is $c(\Lambda_c + \Lambda_a)/1000$ amp. secs., i.e. coulombs. If u and v are the actual velocities of the ions in cms. per sec., under a fall of potential of 1 volt per cm., which is the actual fall of potential in the cell considered, then all the cations within a length of u cm. will pass across a given plane in one direction in 1 second, whilst all the anions within a length of v cms. will pass in the opposite direction. Since the plane has an area of 1 sq. cm., all the cations in a volume

u c.c., and all the anions in a volume v c.c. will pass in opposite directions per second; that is $uc/1000$ and $vc/1000$ gm. equiv. of cations and anions, respectively, are transported per second. Each gm. equiv. carries 96,500 coulombs, that is one faraday (F), and so the quantity of electricity transported per second is $F(uc + vc)/1000$ coulombs. It has been already found independently, however, that the quantity of electricity flowing per second is $c(\Lambda_c + \Lambda_a)/1000$ coulombs; hence these two terms may be equated, thus

$$c(\Lambda_c + \Lambda_a)/1000 = F(uc + vc)/1000$$

$$\therefore \Lambda_c + \Lambda_a = F(u + v) \quad \text{. (vii)}$$

Since it has been shown on p. 71 that

$$\Lambda_c = ku, \text{ and } \Lambda_a = kv$$

it follows that

$$k = F;$$

hence $u = \frac{\Lambda_c}{F} = \frac{\Lambda_c}{96,500}$ cms. per sec. (viii)

and $v = \frac{\Lambda_a}{F} = \frac{\Lambda_a}{96,500}$ cms. per sec. (ix)

under a fall of potential of 1 volt per cm. The absolute velocity of the hydrogen ion at 18°, under these conditions, is given by

$$u_{H^+} = \frac{\Lambda_{H^+}}{96,500} = \frac{315.2}{96,500} = 0.00326 \text{ cms. per sec.}$$

The velocities of other ions, under a fall of potential of 1 volt per cm., have been calculated in a similar manner, and the results are collected in Table XIV. It should be remembered that the absolute velocities calculated by this method are for solutions at *infinite dilution*; in more concentrated solutions the values are probably less, especially for highly ionized strong electrolytes. The velocities, like the ion conductances, vary with the temperature. The results given here are for a potential fall of 1 volt/cm., but the velocity of an ion is directly proportional to the fall of potential.

TABLE XIV

ABSOLUTE VELOCITIES OF IONS AT 18° IN CMS. PER SECOND (CALCULATED)

Ion.	Velocity.	Ion.	Velocity.
Hydrogen	0.00324	Hydroxyl	0.00180
Potassium	0.00066	Sulphate	0.00070
Barium	0.00057	Chlorine	0.00068
Sodium	0.00045	Nitrate	0.00064
Lithium	0.00034	Iodate	0.00035

Experimental Determination of the Absolute Velocity of Ions—The principle of the moving boundary was used by

Lodge* in an attempt to measure the velocities of certain ions; the presence of the ions was indicated by some characteristic property, e.g. colour formation with an indicator, or formation of a precipitate. The apparatus used was of the type shown in Fig. 9; a horizontal tube about 40 cms. long, joining the anode and cathode

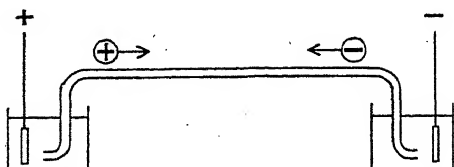


FIG. 9.—Lodge's method for absolute speeds of ions

compartments, contained a conducting gel which held the indicating material. For example in determining the velocity of the barium and chlorine ions the gel contained acetic acid and a trace of silver sulphate; both anode and cathode vessels contained barium chloride solution, and the electrodes were of platinum. On the passage of current both the barium and the chlorine ions travel into the gel and produce visible precipitates of barium sulphate and silver chloride respectively; the rate at which the precipitate proceeds along the tube indicates the velocity of the moving ion. The potential gradient between the electrodes was adjusted so as to be 1 volt per cm., and so the experimental method should give the velocity under these standard conditions. In measuring the speed of the hydrogen ions the gel contained sodium chloride, a little phenol phthalein and a trace of alkali; both vessels contained sulphuric acid, and as the hydrogen ion proceeded in the direction of the current it decolorized the pink phenol phthalein. In Table XIVA are the results obtained for the velocities of some ions; the values calculated from the ion conductances are included for comparison.

TABLE XIVA

ABSOLUTE VELOCITIES OF IONS OBSERVED BY LODGE AND CALCULATED FROM ION CONDUCTANCES (18°)

Ion.	Lodge.	Calculated.
Barium . . .	0.00012 cms./sec.	0.00057 cms./sec.
Strontium . . .	0.00015 „	0.00056 „
Chlorine . . .	0.00024 „	0.00068 „
Bromine . . .	0.00024 „	0.00070 „
Hydrogen . . .	0.0026 „	0.0032 „

Apart from the hydrogen ion values, however, the agreement is very poor. This was probably due, as Whetham† showed, to a

* *Brit. Assoc. Reports*, 1886, 389.

† *Phil. Trans.*, 1893, 184 A, 337.

non-uniform potential gradient and to lack of precautions to obtain sharp boundaries. In Whetham's experiments two solutions with a common ion were used, the non-common ion in one of the solutions being coloured; the specific conductances were almost identical so as to obtain a uniform potential gradient. A sharp boundary was maintained by having the denser solution at the lower level, and also by arranging matters so that the boundary moved in the direction of the solution containing the faster non-common ion (see p. 31). The apparatus is shown diagrammatically in Fig. 10 which is self-explanatory. In subsequent work Whetham* used a similar apparatus for colourless ions; the method of Lodge, including the conducting gel, was used for indicating the boundary. The results given in Table XIVB were obtained at a potential gradient of 1 volt per cm.; they are in better agreement with the calculated values than are those of Lodge.

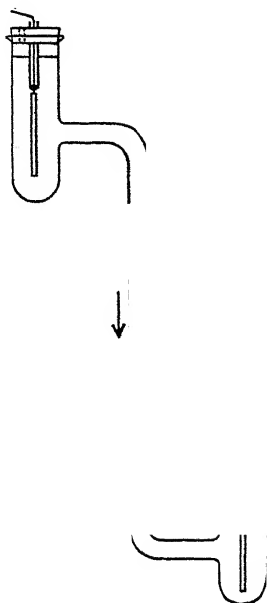


FIG. 10.—Whetham's moving boundary apparatus

TABLE XIVB

ABSOLUTE VELOCITIES OF IONS OBSERVED BY WHEATHAM (18°)

Ion.	Whetham.		Calculated.	
		cms./sec.		cms./sec.
Copper	.	0.00029	.	0.00047
Chlorine	.	0.00058	.	0.00068
Bichromate	.	0.00047	.	0.00047
Barium	.	0.00039	.	0.00057
Calcium	.	0.00035	.	0.00053
Silver	.	0.00049	.	0.00056
Sulphate	.	0.00045	.	0.00070

The methods for determining transport numbers (p. 35) may be used for measuring the absolute velocities of ions provided the fall of potential under which the boundary moves can be evaluated; it is probably in the determination of the potential gradient that the main error in the calculation of velocities arises.† It should also be realized that the values determined from ion conductances are for

* *Ibid.*, 1895, 186 A, 507; see also Smith (S. W. J.), *Proc. Physical Soc.*, 1916, 28, 157.

† For recent studies, see Mukherjee *et al.*, *J. Indian Chem. Soc.*, 1935, 12, 177; 1936, 13, 42.

infinite dilution, whereas the observed results are for appreciable concentrations.

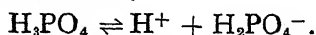
Degree of Dissociation and Conductance Ratio—If all the ions that can be formed from 1 gm. equiv. of an electrolyte take part in the conduction of electricity, the solute is said to be completely dissociated; the equivalent conductance is then equal to Λ_0 , which has been shown to be identical with $F(u + v)$. This condition is only reached in extremely dilute solutions, but in more concentrated solutions it was supposed by Arrhenius that only a fraction α of the gm. equiv. of solute is dissociated into ions. If the velocities of the ions are constant the equivalent conductance of the solution (Λ) is equal to $\alpha F(u + v)$; hence

$$\frac{\Lambda}{\Lambda_0} = \frac{\alpha F(u + v)}{F(u + v)} = \alpha \quad \dots \quad (x)$$

This quantity Λ/Λ_0 has been frequently called the 'degree of ionization' or the 'degree of dissociation' of the electrolyte, but this interpretation depends on the fundamental assumption that the velocities of the ions remain constant. In the first place, apart from other factors, the velocity will be inversely proportional to the viscosity of the solution, and the equivalent conductance may be written as $\alpha F(u + v)\eta_0/\eta$, where η_0 is the viscosity of the solvent and η that of the solution: hence a more accurate value of α would be $\Lambda\eta/\Lambda_0\eta_0$. There are, however, other factors influencing the velocities of the ions. It is commonly accepted at present that strong electrolytes, e.g. strong acids and bases, and most salts, are almost completely ionized at all concentrations, and the decrease of equivalent conductance at increasing concentration is to be attributed not to the decrease in the number of the ions, but to the diminution of speed resulting from inter-ionic and ion-solvent attractions. If these views are accepted it is incorrect to call Λ/Λ_0 the degree of ionization; therefore this fraction is generally given the non-committal name of **conductance ratio**. Although it may have no connection with the number of ions in a solution of a strong electrolyte, it is generally accepted as approximately equal to the degree of dissociation of a weak electrolyte. As a rule the ionic concentration in such electrolytes is so small that the effect of inter-ionic attractions on the speeds of the ions is negligible, and the conductance of the solution is a measure of the number of ions present. A further refinement has been applied* to allow for the small difference between the speeds of the ions in the given weak

* Sherrill and Noyes, *J. Amer. Chem. Soc.*, 1926, 48, 1861; MacInnes, *ibid.*, p. 2068; MacInnes and Shedlovsky, *ibid.*, 1932, 54, 1429; 1925, 57, 1705; Saxton *et al.*, *ibid.*, 1933, 55, 3638; 1934, 56, 1918; Brockman (F. G.) and Kilpatrick (M.), *ibid.*, p. 1483; Jeffery and Vogel (A. I.), *J. Chem. Soc.*, 1932, 2829; 1933, 1637; 1934, 21.

electrolyte and at infinite dilution. Instead of comparing Λ with Λ_0 , the latter is replaced by the equivalent conductance the electrolyte would have if completely ionized at the same *ionic* concentration as in the experimental solution. The method of evaluation is best illustrated by an example; in the case of phosphoric acid, ionizing as a monobasic acid,



By Kohlrausch's law of independent migration

$$\Lambda_{\text{H}_3\text{PO}_4} = \Lambda_{\text{NaH}_2\text{PO}_4} + \Lambda_{\text{HCl}} - \Lambda_{\text{NaCl}},$$

and the values at infinite dilution are

$$\begin{aligned}\Lambda_{\text{H}_3\text{PO}_4} &= 70.0 + 378.3 - 109.0 \\ &= 339.3 \text{ recip. ohms.}\end{aligned}$$

The measured value of Λ for H_3PO_4 at a concentration of 0.1 gm. equiv. per litre is 96.5; hence the approximate degree of dissociation is $96.5/339.3$, i.e. 0.285, and the *ionic* concentration is approximately 0.0285. The equivalent conductances of NaH_2PO_4 , HCl and NaCl are then found, from published data, at this ionic concentration, complete ionization being assumed in these strong electrolytes. The values are 59.3, 363.4 and 98.6; hence $\Lambda_{\text{H}_3\text{PO}_4}$, if completely ionized at a concentration of 0.0285, would be

$$59.3 + 363.4 - 98.6 = 324.1.$$

The more accurate value of the degree of dissociation is therefore $96.5/324.1$, that is 0.298. With more concentrated solutions or with stronger acids the difference between the approximate (conductance ratio) and corrected degrees of dissociation is greater than in the example quoted.*

The conductance ratios at 18° for a number of salts, acids and bases at various dilutions have been collected in Table XV (p. 80); it may be observed that salts of the same valence type generally have almost identical conductance ratios, especially in dilute solutions. Salts of higher valence types generally have smaller ratios than do uni-univalent electrolytes at the same dilutions. It is clear, too, that weak electrolytes, e.g. acetic acid and ammonia, can be placed in a separate category from strong acids and bases, and most salts.

Influence of Temperature on Conductance—It has been seen that the velocity of an ion increases as the temperature is raised, hence at infinite dilution the equivalent conductances must increase. A formula of the same type as that applicable to ion conductances must, of course, be used, viz.

$$\Lambda_t = \Lambda_{18}[1 + c(t - 18)]$$

* For a method of correcting for the speeds of the ions based on the Onsager equation, see p. 162.

TABLE XV

CONDUCTANCE RATIOS AT VARIOUS CONCENTRATIONS (18°) *

Electrolyte.	Normality.			
	0.001	0.01	0.1	1.0
Sodium Chloride . . .	0.977	0.936	0.852	0.741
Potassium Iodide . . .	0.978	0.941	0.869	0.727
Sodium Nitrate . . .	0.977	0.932	0.832	0.660
Lithium Iodate . . .	0.970	0.912	0.789	0.643
Calcium Chloride . . .	0.954	0.882	0.764	0.662
Strontium Nitrate . . .	0.953	0.871	0.719	0.511
Lead Nitrate . . .	0.947	0.845	0.635	0.377
Barium Bromate . . .	0.947	0.856	—	—
Potassium Sulphate . . .	0.954	0.872	0.722	0.592
Potassium Oxalate . . .	0.960	0.886	0.753	0.643
Copper Sulphate . . .	0.862	0.629	0.396	0.309
Cadmium Sulphate . . .	0.850	0.614	0.377	0.277
Hydrochloric Acid . . .	0.988	0.972	0.925	0.79
Potassium Hydroxide . . .	0.99	0.96	0.90	0.77
Acetic Acid . . .	0.117	0.041	0.013	0.0038
Ammonium Hydroxide . . .	0.118	0.042	0.014	0.0037

where c , the temperature coefficient, is equal to $(c_u\Lambda_c + c_v\Lambda_a)/(\Lambda_c + \Lambda_a)$, the terms c_u and c_v being the ion conductance temperature coefficients for cation and anion respectively. This straight line conductance-temperature relationship does not hold at low temperatures, the decrease of conductance being less than required by the formula; the conductance-temperature curve appears to become asymptotic with the temperature axis.† Since weak electrolytes probably have a definite heat of ionization in solution an increase of temperature will cause a decrease in the degree of ionization, and hence in the conductance ratio; this will tend to oppose the increased conductance due to the increased velocity of the ions. It is therefore to be expected that some electrolytes will have a maximum equivalent conductance at a certain temperature; such maxima have been observed both in aqueous and non-aqueous solutions, particularly when concentrated. Some of the results obtained by Noyes and his collaborators ‡ for conductance ratios at elevated temperatures are quoted in Table XVI.§

* Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, 34, 454.

† See Bousfield and Lowry (T. M.), *Proc. Roy. Soc.*, 1902, 71 A, 42.

‡ *Carnegie Publications*, 1907, No. 63; *J. Amer. Chem. Soc.*, 1910, 32, 159. For methyl alcohol and acetone solutions, see Blokker, *Rec. trav. chim.*, 1935, 54, 975.

§ For further details see Kraus, *Electrically Conducting Systems*, 1922, Chap. VI. Fuoss, *J. Amer. Chem. Soc.*, 1934, 56, 1855, has given a theoretical derivation of the temperature coefficient of conductance in solvents of low dielectric constant.

TABLE XVI

CONDUCTANCE RATIOS AT ELEVATED TEMPERATURES
(CONCENTRATIONS 0.01 AND 0.08N)

	18° 0.01N 0.08N		100° 0.01N 0.08N		156° 0.01N 0.08N		218° 0.01N 0.08N		306° 0.01N 0.08N	
Hydrochloric Acid. .	0.97	0.93	0.95	0.90	0.94	0.87	0.92	0.82	0.82	0.60
Nitric Acid . .	0.97	0.93	0.95	0.89	0.93	0.85	—	0.75	—	0.33
Sodium Hydroxide .	0.96	—	0.96	—	0.94	—	0.92	—	—	—
Potassium Chloride .	0.94	0.87	0.91	0.83	0.90	0.80	0.90	0.77	0.81	0.64
Silver Nitrate . .	0.93	0.83	0.92	0.80	0.89	0.76	0.86	0.71	0.77	0.57
Barium Hydroxide .	0.93	0.83	0.85	0.70	0.85	0.65	—	—	—	—
Potassium Sulphate .	0.87	0.73	0.80	0.65	0.75	0.58	0.63	0.45	0.37	0.23
Magnesium Sulphate .	0.67	0.45	0.52	0.32	0.35	0.19	0.13	0.07	—	—
Phosphoric Acid . .	0.60	0.31	0.42	0.19	0.29	0.12	—	—	—	—
Acetic Acid. . .	0.04	0.015	0.03	0.012	0.023	0.008	0.013	0.005	—	0.0014
Ammonium Hydroxide	0.04	0.015	0.036	—	0.025	—	0.014	0.005	—	0.0011

Influence of Pressure on Conductance—The effect of pressure on conductance is the resultant of four factors : (a) the volume change of the solution on compression ; (b) the change in mobility of the ions due to changes in viscosity, size of ion complex, and inter-ionic forces ; (c) the change in degree of ionization of the electrolyte ; and (d) the change in conductance of the solvent.* For a fairly dilute solution of a strong electrolyte the influence of the last two factors is negligible, and only the first two need be considered. The change in volume of a dilute solution on compression is almost the same as that of the pure solvent ; for a given dilute solution the influence of pressure should thus depend mainly on the variation of ionic speed. If the size of the ion remains constant the speed should be inversely proportional to the viscosity, and the conductance of a given solution should vary with pressure in a manner parallel to the viscosity. The viscosity of a solution is, in general, decreased by increase of pressure ; † this effect is greater with dilute solutions at low temperatures. With concentrated solutions increase of pressure may cause an increase of viscosity ; even in dilute solutions at very high pressures there is a reversal of the effect and the viscosity increases. In accordance with these observations it has been found that the conductance of a solution increases at first with increasing pressure, especially at low temperatures ; at high pressures the conductance decreases after reaching a maximum value. ‡ The conductance change does not appear to be quite inversely proportional to the viscosity change ; hence other factors probably affect the ionic velocities. It is possible that

* Tammann, *Z. physikal. Chem.*, 1898, 27, 458.† Cohen, *Ann. Physik*, 1892, 45, 666.‡ Körber, *Z. physikal. Chem.*, 1909, 67, 212 ; Tammann and Rohmann, *Z. anorg. Chem.*, 1929, 183, 1 ; Adams (L. H.) and Hall (R. E.), *J. Physical Chem.*, 1931, 35, 2145.

the effective size of the ion-solvent complex may vary with the pressure,* and the inter-ionic forces may also change.

For weak electrolytes the influence of pressure on the degree of ionization is of importance. It has been found that an aqueous solution decreases in volume as a result of the ionization of the solute; † increase of pressure will therefore favour ionization. In agreement with this view it has been found ‡ that the conductance of a weak electrolyte increases much more rapidly with increasing pressure than does that of a strong electrolyte; in the former case both viscosity and ionization factors are operative.§

Non-Aqueous Solutions—Hitherto more specific reference has been made to aqueous solutions, but many non-aqueous solvents are capable of forming solutions which conduct the electric current. The behaviour of the solutions is often complex, and although a great deal of investigation has been made in connection with them,|| our knowledge is very far from complete. It is on account of the anomalous behaviour sometimes observed with non-aqueous solutions that they are dealt with separately. According to Walden *all* solvents are capable of causing dissolved electrolytes to dissociate to a greater or lesser extent,** but, in general, highly associated solvents with a high dielectric constant are the best dissociating media. Other factors, of a purely chemical nature, are often, however, of considerable importance.

Conductance—The determination of the conductance of non-aqueous solutions is not so simple as for aqueous solutions, since the specific conductance is generally lower and decomposition of the solvent is more liable to occur. The experimental technique has been studied by Morgan and Lammert; †† these authors have

* Zisman, *Physical Rev.*, 1932, 39, 151.

† Drude and Nernst, *Z. physikal. Chem.*, 1894, 14, 536.

‡ Fanjung, *ibid.*, 1894, 14, 673; Körber, *loc. cit.*, Tammann and Tofaute, *Z. anorg. Chem.*, 1929, 182, 353; Adams and Hall, *loc. cit.*

§ For further details see Kraus, *op. cit.*, p. 126 *et seq.*; Taylor, *Physical Chemistry*, 1931, p. 668 (Partington).

|| For full account, see Kraus, *op. cit.*; Walden, *Elektrochemie nicht-wässriger Lösungen*, 1924; *Salts, Acids and Bases* (George Fisher Baker Lectures, 1929); Müller (R.), 'Elektrochemie der nichtwässrigen Lösungen', *Ahren's Sammlung*, 1924, 27; Hartley (H.) and others, *Ann. Reports*, 1930, 27, 326; Davies, *The Conductivity of Solutions*, 1933; Wien-Harms, *Handbuch der Experimentalphysik*, 1932, XII, Part I (Ebert); Eucken-Wolf, *Hand- und Jahrbuch der Chemischen Physik*, 1933, Vol. 6, Section II, B (Ulich). For more recent work, see papers by Hartley (H.), Kraus, Partington, Philip, Walden and their collaborators.

** *Z. physikal. Chem.*, 1906, 54, 129.

†† *J. Amer. Chem. Soc.*, 1923, 45, 1692; see also Murray-Rust and Hartley (H.), *Proc. Roy. Soc.*, 1929, 126 A, 84. For the study of solutions of very low conductivity a direct current method has been described by Kraus and Fuoss, *J. Amer. Chem. Soc.*, 1933, 55, 21.

designed cells specially for use with non-aqueous solutions, and have described the precautions which must be taken in order to obtain reliable results. The lack of due care in conductance measurements invalidates many of the results found in the literature, but in spite of this it is possible to draw certain general conclusions. For solvents with good dissociating power the equivalent conductance increases with increasing dilution as is the case with aqueous solutions. The results quoted in Table XVII illustrate this similarity; they are obtained from the work of Philip and Oakley,* using nitromethane (dielectric constant, 39) as solvent, and from that of Martin † with benzonitrile (dielectric constant, 26).

TABLE XVII

EQUIVALENT CONDUCTANCES IN NON-AQUEOUS SOLUTIONS AT 25°

KI in nitromethane.		AgNO ₃ in benzonitrile.	
Dilution (litres).	Λ	Dilution (litres).	Λ
82.9	85.1	100	10.5
200.9	98.1	500	19.3
408.0	105.5	1,000	24.7
740.2	111.7	2,000	30.6
1,673	115.8	5,000	37.6
4,915	119.3	10,000	42.0
10,082	120.5	20,000	45.4

In many cases, however, the results are quite different; this is particularly so with solvents of low dielectric constant. For example, the equivalent conductance of potassium iodide in liquid sulphur dioxide at first increases with increasing dilution, reaches a maximum and then commences to decrease; on further dilution the equivalent conductance after passing through a minimum increases steadily towards a limiting value at infinite dilution. The values obtained by Franklin ‡ are given in Table XVIII.

TABLE XVIII

EQUIVALENT CONDUCTANCE OF POTASSIUM IODIDE IN LIQUID SO₂ AT -10°

Dilution	0.5	1.0	2.0	4.0	8.0	16	64	128	512	2,000	8,000
Λ	39.7	46.9	46.8	44.8	42.5	43.5	55.7	66.5	99.2	140.5	181.8

Similar cases have been found with other solvents,§ and there are also many instances of a minimum in the equivalent conductance at a certain dilution, e.g. mercuric and silver cyanides in liquid ammonia, hydrochloric acid in ether and in iso-amyl alcohol. In

* *J. Chem. Soc.*, 1924, 125, 1189.† *Ibid.*, 1928, 3270.‡ *J. Physical Chem.*, 1911, 15, 675.§ The maxima reported for certain aqueous solutions are probably due to experimental errors, see Berthoud, *Helv. Chim. Acta*, 1930, 13, 17.

some instances the equivalent conductance appears to decrease steadily with increasing dilution, e.g. tetra-methyl-ammonium chloride in bromine.* The abnormalities have been attributed to (a) complex formation between solute and solvent, i.e. solvation; † (b) variation of the dielectric constant with the concentration, e.g. dielectric constant of chloroform is 4.95, but for a *N*-solution of tetra-ethyl-ammonium chloride in chloroform it is 28.8; (c) association of solute molecules; ‡ (d) decomposition of the solute by the solvent; § and (e) probably most important of all, interaction between the ions themselves and between ions and molecules of solute. || Walden ** has found that for a solvent of dielectric constant *D* the equivalent conductance of a given electrolyte is a minimum at a concentration $c_{\min.}$ such that

$$D^3/c_{\min.} = \text{a constant.} \dagger\dagger$$

From this relationship it may be seen that if the dielectric constant of the solvent is high the minimum can only be observed in very concentrated solutions; in such circumstances other factors operate which tend to obscure the minimum. Kraus and Fuoss ‡‡ studied the conductivity of solutions of tetra-isoamyl-ammonium nitrate in a series of mixtures of dioxan and water, the dielectric constants of which varied regularly from 2.2 to 78.6; the conductivity minimum was found to move to regions of higher concentration as the dielectric constant of the medium was increased. In solvents of very low or high dielectric constant the minimum probably occurred at such low or high concentrations, respectively, that it could not be observed.

Equivalent Conductance at Infinite Dilution—For strong electrolytes the value of Λ_0 may be obtained by the extrapolation methods described in connection with aqueous solutions (p. 68); as a general rule the equivalent conductance varies in a linear

* See Darby, *J. Amer. Chem. Soc.*, 1918, 40, 347.

† Steele and McIntosh, *Proc. Roy. Soc.*, 1905, 74 A, 321; Steele, McIntosh and Archibald, *Z. physikal. Chem.*, 1906, 55, 129; Archibald, *J. Amer. Chem. Soc.*, 1907, 29, 665; Plotnikov, *et al.*, *Z. physikal. Chem.*, 1935, 172, 304. See Kraus and Fuoss, *loc. cit.*, for further references.

‡ Walden, *Z. physikal. Chem.*, 1920, 94, 352.

§ Cf. Jones (H. C.) and Lindsay, *Amer. Chem. J.*, 1902, 28, 329; Walden, *Z. physikal. Chem.*, 1905, 54, 144.

|| Gross (P.) and Halpern, *Physikal. Z.*, 1925, 26, 636; La Mer and Downes, *J. Amer. Chem. Soc.*, 1931, 53, 888; Fuoss and Kraus, *ibid.*, 1933, 55, 2387.

** *Z. physikal. Chem.*, 1922, 100, 512.

†† It has been shown by Fuoss and Kraus, *loc. cit.*, that this relationship may have a theoretical basis (see p. 172).

‡‡ *J. Amer. Chem. Soc.*, 1933, 55, 21; for references to work by these authors with solvents of low dielectric constant, see p. 156 *supra*.

manner with the square-root of the concentration, as required by the Kohlrausch formula (equation viii, p. 68) and the Debye-Hückel-Onsager equation (Chapter VII).^{*} In some cases the cube-root formula of Kohlrausch (p. 68) is more suitable for extrapolation purposes,[†] whereas in others the general formula of Ferguson and Vogel may be used.[‡] For some solutions, e.g. tetra-methyl-ammonium chloride in bromine, it is impossible to determine a value of Λ_0 , since the equivalent conductance decreases with increasing dilution, and in other cases the extrapolation is very uncertain. A method of evaluating Λ_0 applicable to many media of low dielectric constant is considered later (p. 165).

Viscosity and Equivalent Conductance—If the radius of an ion is independent of the nature of the solvent, and Stokes' law may be applied, it follows that the speed of the ion multiplied by the viscosity of the medium should be constant. Since the equivalent conductance at infinite dilution depends only on the speeds of the ions, then for a given electrolyte the product of equivalent conductance and the viscosity of the solvent should be independent of the solvent; that is, $\Lambda_0\eta_0$ should be a constant for a given solute in all solvents. This relationship was suggested by Walden § as a result of his work on the conductance of tetra-ethyl-ammonium iodide in various solvents, and confirmation has been claimed more recently || as a consequence of further investigation. As a corollary of the Walden rule the product of ion conductance and viscosity of the medium should also be a constant. An examination of the published measurements, however, shows that the conductance-viscosity product is only approximately constant; water, particularly, gives very divergent results. It is very doubtful, therefore, if ions can be regarded as having the same effective diameter in all solvents; when 'chemical' solvation occurs divergences must result. The data in Table XIX are taken from the compilations of Ulich ** and of Barak and Sir Harold Hartley; †† they show the general tendency of the ion conductance-viscosity product.

* This has been amply verified by measurements in various solvents made by Hartley (H.) and Walden, and their collaborators; see references, p. 161.

† Cf. Hawkins and Partington, *Trans. Faraday Soc.*, 1928, 24, 529.

‡ Martin, *loc. cit.*

§ *Z. physikal. Chem.*, 1906, 55, 207, 246.

|| Walden *et al.*, *ibid.*, 1923, 107, 219; 1925, 114, 297; 1926, 113, 429; *Salts, Acids and Bases*, 1929; and numerous papers in the *Z. physikal. Chem.*, by Walden and collaborators, e.g. 1933, 165, 11, 26, 32. Also, see Philip and Rangaramanujam, *J. Chem. Soc.*, 1932, 1512; Coates and Taylor (E. G.), *ibid.*, 1936, 1245; for summaries, see Ulich, *Fortschritte der Chemie, Physik und physikal. Chem.*, 1926, 18, No. 10; *op. cit.*, p. 147; *Trans. Faraday Soc.*, 1927, 23, 388.

** *loc. cit.*

†† *Z. physikal. Chem.*, 1933, 165, 273.

TABLE XIX

VALUES OF PRODUCT OF ION CONDUCTANCES AND VISCOSITY AT 25°

Solvent	Ion.							
	H+.	Li+.	Na+.	NH ₄ +.	N(C ₂ H ₅) ₄ +	Cl-.	Br-.	NO ₃ -.
Water	3.14	0.36	0.46	0.66	0.294	0.69	0.70	0.63
Methyl alcohol	0.78	0.22	0.26	0.32	0.338	0.29	0.30	0.83
Ethyl alcohol	0.67	0.16	0.20	0.20	0.307	0.26	0.24	0.28
Acetone	—	0.22	0.22	0.28	0.294	0.33	0.37	—
Acetonitrile	—	—	0.28	—	0.294	—	0.35	—

The difference in the conductances of potassium chloride and acetate in light and heavy water is mainly due to the change in viscosity of the medium; with acids, however, this relationship does not apply because of the abnormal behaviour of the hydrogen ion * (*vide infra*).

Transport Numbers.—Transport numbers in non-aqueous solutions have been determined by methods similar to those used for aqueous solutions; the results are on the whole of the same type, although variations with concentration are more marked.† If the velocity of an ion is inversely proportional to the viscosity, then the transport numbers of the ions of any electrolyte, in dilute solutions, should be independent of the nature of the solvent. This can only be approximately true, as the figures given in Table XIX clearly indicate. The work of Birkenstock‡ shows that anomalous cases exist; thus the anion transport numbers for lithium chloride, bromide and iodide solutions in acetone are 1.21, 0.833 and 0.614 respectively. These abnormal results with lithium chloride are similar to those observed with cadmium iodide in aqueous solution, and Birkenstock concludes that complexes are formed in acetone solution. Clearly if this type of complex formation occurs the Walden rule cannot apply.

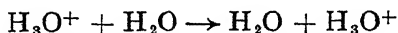
Grotthuss Chains.—It will be observed from Table XIX that the ion conductance, and consequently the transport number, of the hydrogen ion is abnormally high in aqueous solution; since this ion is certainly hydrated, with at least one molecule of water, e.g. H₃O⁺, the product of ion conductance and viscosity is greater than is to be expected. In recent years there has been a growing

* La Mer *et al.*, *J. Physical Chem.*, 1935, 3, 406; *J. Amer. Chem. Soc.*, 1936, 58, 1642.

† For references, see Walden, *Elektrochemie nichtwässeriger Lösungen*, 1924, Chap. VI; Hartley (H.) *et al.*, *Ann. Reports*, 1930, 27, 346; Taylor, *Physical Chemistry*, 1931, 727 (Partington).

‡ *Z. physikal. Chem.*, 1928, 138, 432; see also Koch, *J. Chem. Soc.*, 1928, 524.

conviction * that in water, and probably to some extent in other hydroxylic solvents, e.g. methyl and ethyl alcohols, ordinary electrical transport is not solely responsible for the conducting power of the hydrogen ion, but that a form of Grotthuss conductivity (cf. p. 14) is operative to a considerable extent. If a proton, that is an unsolvated hydrogen ion, is able to pass from a H_3O^+ ion to a water molecule, thus



by purely chemical interchange, a process has occurred resulting in the transport of electricity which is independent of the velocity of the hydrogen ion. The interchange depicted above, taking place along a whole chain of water molecules, will lead to considerable conductivity, much greater than would be expected for a normal ion. An analogous process probably accounts for the high conductivity of the hydroxyl ion in aqueous solution.

Nature of Solvent and Conductance Ratio—It was suggested, on theoretical grounds, by Thomson † and by Nernst ‡ that solvents with high dielectric constants should have the greatest dissociating influence on an electrolyte; this is generally known as the Nernst-Thomson rule. The force of attraction between two electric charges of opposite sign is given by the equation $F = e_1 e_2 / Dd^2$, where e_1 and e_2 are the magnitudes of the charges, d their distance apart, and D the dielectric constant of the medium; the greater the value of D the smaller the electrostatic force holding the charges together. According to modern views of valency § an electrolyte consists of a positive ion and a negative ion, generally held together by electrostatic forces only; if the substance is dissolved in a medium of high dielectric constant the inter-ionic attractive force is reduced, and the ions become free to move under the influence of an applied *E.M.F.* It is to be expected, therefore, that for a given concentration of electrolyte the conductance ratio will be higher in a solvent of high dielectric constant; a theoretical connection has, in fact, been deduced on the basis of the Debye-Hückel theory (p. 157). For weak electrolytes the degree of ionization probably increases to some extent with increasing dielectric constant, but as already indicated the chemical nature of the solvent is often of importance (see Chapter VII).

* See, for example, Hückel, *Z. Electrochem.*, 1928, **34**, 346; Huggins, *J. Amer. Chem. Soc.*, 1931, **53**, 3190; Bernal and Fowler, *J. Chem. Physics*, 1933, **1**, 515; Baker and La Mer, *ibid.*, 1935, **3**, 401; Wannier, *Ann. Physik*, 1935, **24**, 543, 569.

† *Phil. Mag.*, 1893, **36**, 320.

‡ *Gött. Nach.*, 1893, No. 12; *Z. physikal. Chem.*, 1894, **13**, 531.

§ See Sidgwick, *The Electronic Theory of Valency*.

For strong electrolytes Walden* has suggested the empirical relationship that the conductance ratio is the same in different solvents when the product of the dielectric constant and the cube-root of the dilution is the same in each solvent; that is, for a given conductance ratio, $D\sqrt[3]{v}$ is a constant, where D is the dielectric constant of the solvent and v the dilution of the solution. This relationship is, however, only approximate; Kraus† has pointed out many exceptions and considers the apparent agreement to be fortuitous. Fredenhagen and Dahmlos‡ have shown that conductance ratios in hydrogen cyanide solutions are very much lower than in aqueous solutions, in spite of the higher dielectric constant of the former solvent. As a result of a comprehensive survey of the subject, Walden and Hilgert§ have concluded that the connection between conductance ratio and dielectric constant given above is applicable to 'levelling' solvents (see p. 176), mostly of the hydroxylic type, but breaks down with others, e.g. nitriles and ketones. Some values for the conductance ratio of tetra-ethyl-ammonium iodide in various solvents have been collected in Table XX; they show that dielectric constant cannot be the only factor influencing the freedom of the ions. Attempts have also been made to correlate ionizing power with the factor of association of the solvent; || recently the ability of a solvent to 'donate' electrons has been suggested as a criterion of its ionizing power.**

TABLE XX

DIELECTRIC CONSTANT (D) OF MEDIUM AND CONDUCTANCE RATIO (α) OF TETRA-ETHYL-AMMONIUM IODIDE IN 0.01*N*-SOLUTION

Solvent.	D .	α	Solvent.	D .	α
Formamide	84	0.93	Acetone	21	0.50
Water	81	0.91	Propionaldehyde	18	0.55
Nitromethane	39	0.78	Acetic anhydride	18	0.58
Acetonitrile	36	0.71	Acetyl chloride	15.5	0.46
Benzonitrile	26	0.61	Salicylaldehyde	13.9	0.34

Mixed Solvents ††—Although a great many measurements have

* *Z. physikal. Chem.*, 1906, 54, 131; 1920, 94, 263; 1930, 147, 1.

† *op. cit.*, pp. 93, 94; see also, van Arkel and Snoek, *Rec. trav. Chim.*, 1934, 53, 675.

‡ *Z. anorg. Chem.*, 1929, 179, 77; see also Kahlenberg and Schlundt, *J. Physical Chem.*, 1902, 6, 447.

§ *Z. physikal. Chem.*, 1933, 165, 241.

|| See Turner, *J. Chem. Soc.*, 1911, 99, 880.

** Hunt and Briscoe, *J. Chem. Ed.*, 1929, 6, 1716; see also Wynne-Jones, *J. Chem. Soc.*, 1931, 795; and Chap. VII.

†† See Taylor, *Physical Chemistry*, 1931, p. 728 (Partington) for many references; Davies, *op. cit.*, Chap. XII; Brownson and Cray, *J. Chem. Soc.*, 1925, 127, 2923; Whitman and Spencer, *J. Amer. Chem. Soc.*, 1928, 50, 1840; Kraus and Fuoss, *loc. cit.*; Connell, Hamilton and Butler,

been made on the conductance of various electrolytes in mixed solvents the results are so complex that it is difficult to draw any definite conclusions from them. In most cases the dielectric constant of a mixture lies between the values for the separate constituents; hence the ionizing power should also be roughly intermediate. The extent to which a given solute forms complexes with one solvent is greatly influenced by the presence of another, e.g. Birkenstock* found that the addition of methyl alcohol destroyed the lithium halide complexes in acetone; the conductance of the solution in the mixed solvent may thus be very different from that in a single solvent. Even if the nature of the ion-complex is not appreciably affected by alteration of the solvent, the viscosity of the latter will have an effect on the ionic velocity. The viscosity of a mixture of two liquids may vary continuously between the values for the individual viscosities of the components as the composition is altered, or else the viscosity-composition curve may show a maximum or a minimum; similar and parallel variations are often found in the conductances in mixed solvents. The viscosity of acetone-water mixtures is a maximum at 40 per cent. of acetone; in agreement with this it is found that the conductances for several salts, e.g. potassium chloride and iodide, and lithium bromide, show distinct minima when dissolved in a series of acetone-water mixtures. These minima occur at 60, 50 and 55 per cent. of acetone, respectively; hence although there is a parallelism between viscosity and conductance the proportionality is not exact, and other factors must be operative. For calcium nitrate solutions in acetone-water mixtures the connection between viscosity and conductance breaks down completely, especially as the conductance is greater in water, although its viscosity is greater than that of acetone. Similarly, the viscosity of ethyl alcohol-water mixtures is a maximum at about 45 per cent. of alcohol, but the conductance of lithium nitrate solutions in such mixtures increases regularly from pure ethyl alcohol to pure water. The equivalent conductance of both lithium chloride and potassium iodide is inversely proportional to the viscosity in ethyl alcohol-water mixtures containing up to 20 mols. per cent. of alcohol, but beyond this increasing divergences are found.† This result is accounted for by the increasing solvation of the ions by molecules of ethyl alcohol; analogous solvates may account for the results with lithium nitrate. The conductance of an electrolyte in a mixed solvent may, therefore, depend on the dielectric constant of the medium, its viscosity and the specific influence of each constituent of the solvent on the ions.

Proc. Roy. Soc., 1935, 147 A, 418; Agarwalla and Manderville, *J. Indian Chem. Soc.*, 1935, 12, 699.

* *loc. cit.*

† Connell, Hamilton and Butler, *loc. cit.*

The effect of small amounts of water, less than 0.5 per cent., is often of interest and has helped to throw some light on the nature of the ionization process in a given solvent.* With highly ionized salts the change of conductivity generally corresponds to the alteration in the viscosity, irrespective of the nature of the solvent, but with strong acids, which are also highly ionized, the decrease of conductance in alcoholic solvents is much greater than is to be expected although it is normal in acetone. It may be observed that there is probably no Grotthuss conduction by the hydrogen ion in the latter solvent, whereas it probably does occur in the alcohols. The greater affinity of the water molecules for the proton apparently hinders the transfer from one molecule of alcohol to another in a Grotthuss chain (p. 87). The conductance of a weak electrolyte is generally increased by the addition of a small amount of water to an extent far in excess of that to be anticipated from the increase of dielectric constant.†

Applications of Conductance Measurements. Conductometric Titrations ‡—In addition to the uses of conductance measurements in the control of industrial processes,§ there are a number of laboratory applications. Kohlrausch || suggested that conductance measurements could be utilized to determine the end-point of a neutralization reaction; this application depends on the high mobility of the hydrogen and hydroxyl ions, and the consequent high conductance of free strong acid and alkali. If an alkali is added to an acid solution the latter is removed by neutralization; as the salt formed has a lower conductance than the acid, the conductivity of the solution falls. When neutralization is complete the further addition of alkali causes the conductance to increase. At the neutral point, therefore, it will be a minimum, and a curve in which the conductance of the solution is plotted against the volume of alkali added will be of the form of Fig. 11 (I), if both acid and alkali are strong; the neutralization-point is at C. In

* For summary of results, see Hartley (H.) *et al.*, *Ann. Reports*, 1930, 27, 353; see also Hughes (O. L.) and Hartley (H.), *Phil. Mag.*, 1933, 15, 610; Kolthoff and Willman, *J. Amer. Chem. Soc.*, 1934, 56, 1007.

† See, for example, Hartley (H.) *et al.*, *J. Chem. Soc.*, 1931, 199.

‡ For reviews and references, see Kolthoff, *Konduktometrische Titrationen*, 1923; *Ind. Eng. Chem. (Anal. Ed.)*, 1930, 2, 225; Davies, *The Conductivity of Solutions*, 1933, Chap. XIX; Glasstone, *Ann. Reports*, 1933, 30, 294; Britton, *Conductometric Analysis*, 1934; Jander and Pfundt, *Leitfähigkeits-titrationen und Leitfähigkeitsmessungen*, 1934; Böttger, *Physikalische Methoden der analytischen Chemie*, 1935, Part II (Jander and Pfundt); see also, Pieper, *Z. Elektrochem.*, 1934, 40, 544; Harms and Jahr, *ibid.*, 1935, 41, 130; and discussion, *ibid.*, pp. 453 and 457.

§ Keeler, *Trans. Amer. Electrochem. Soc.*, 1920, 38, 113; Parker (H.C.), *Ind. Eng. Chem.*, 1927, 19, 660; Böttger, *op. cit.*, article by Sändera.

|| *Ann. Physik*, 1885, 26, 225.

order to simplify the method the volume of alkali may be plotted against the reading on the Wheatstone bridge (Fig. 6), if the resistance R is kept constant. Straight lines may be drawn through points so obtained, six or eight values are sufficient, and the end-point is given by their position of intersection; alternatively, it may be obtained by calculation.* The most accurate results are obtained when there is little volume change during the titration; if the alkali is about ten times as concentrated as the acid the conditions are satisfactory.

When necessary one of the solutions may be diluted before titration, and the reaction may be carried out in either direction. According to Küster,† who made some of the earliest conductometric titrations, the method is capable of considerable accuracy, provided other electrolytes are absent.‡ Solutions of acids as dilute as 0.001*N* may be estimated by the conductivity method.

When a moderately weak acid, e.g. acetic acid, is titrated with a strong base then, owing to the effect of the common anion in repressing the dissociation (p. 101), the conductivity of the solution falls somewhat at the commencement of neutralization, but the conducting power of the highly ionized salt soon exceeds that of the weak acid which it replaces and the conductance increases. Immediately the end-point is passed a more rapid increase results because of the high mobility of the hydroxyl ions from the alkali. The conductivity-titration curve is of the form of Fig. 11 (II), the end-point being at the intersection of the two lines. If the acid is very weak, e.g. a phenol or boric acid, the conductance of the original solution is very small and it rises from the beginning

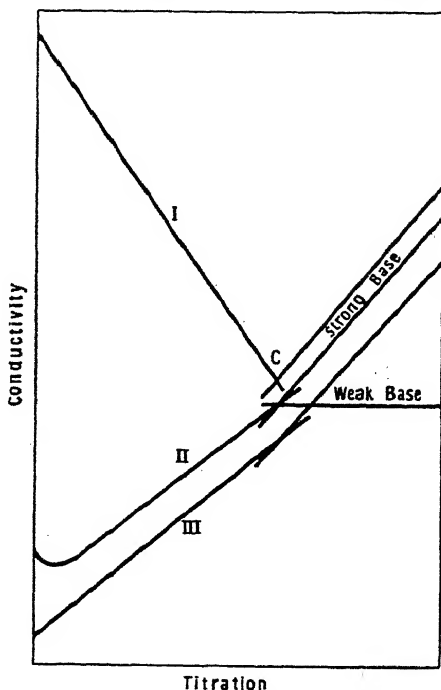


FIG. 11.—Conductometric titration curves

tion, but the conducting power of the highly ionized salt soon exceeds that of the weak acid which it replaces and the conductance increases. Immediately the end-point is passed a more rapid increase results because of the high mobility of the hydroxyl ions from the alkali. The conductivity-titration curve is of the form of Fig. 11 (II), the end-point being at the intersection of the two lines. If the acid is very weak, e.g. a phenol or boric acid, the conductance of the original solution is very small and it rises from the beginning

* Boulad, *Bull. Soc. Chim.*, 1936, 3, 408.

† *Z. anorg. Chem.*, 1903, 35, 454; 1904, 42, 225.

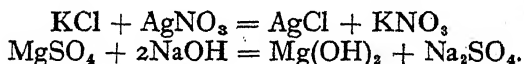
‡ See, however, Jander and Ebert, *Z. Elektrochem.*, 1935, 41, 790.

of the titration, as in Fig. 11 (III). The sharpness of the break at the end-point, upon which the accuracy of the estimation depends, may be improved by using a weak base, e.g. ammonia, as titrant with moderately weak acids; the first part of the titration curve is similar to that for a strong base, but after the end-point it is almost horizontal because the weak base is a poor conductor, although its salts have a high conductivity. Moderately strong acids, e.g. mandelic acid, give titration curves of a type intermediate between those for weak and strong acids and their shape is such that the graphical determination of the end-point with any degree of accuracy is not possible: for these acids special procedures must be adopted.* A mixture of a strong and a weak acid can be readily analysed by the conductometric method, preferably using a weak base as titrant. The conductance first decreases as the strong base is neutralized, and when this process is complete it increases, as is general with a weak acid; finally neutralization of both acids is indicated by the conductivity becoming almost constant.

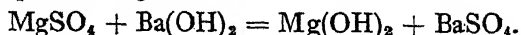
Conductometric titration may be used to determine the end-point in displacement reactions, e.g. sodium acetate and hydrochloric acid:



In this case the addition of hydrochloric acid has very little influence on the conductance, until the end-point is reached, since the values for sodium chloride and acetate are very similar; the conductivity then rises suddenly as the free strong acid is now present. Similar curves are obtained for precipitation reactions,† e.g.



It is sometimes advantageous to employ an alcoholic medium in which the solubility of the precipitate is diminished.‡ In the reaction between the sulphate of a metal yielding a sparingly soluble hydroxide and barium hydroxide, both reaction products separate from solution and the conductance falls until the sulphate is completely precipitated, e.g.



* Kolthoff, *Z. anorg. Chem.*, 1920, 111, 11; Righellato and Davies, *Trans. Faraday Soc.*, 1933, 29, 429. For an estimate of the difference between true and observed end-points for acids and bases of different strengths, see Eastman, *J. Amer. Chem. Soc.*, 1925, 47, 332.

† Dutoit, *J. Chem. physique*, 1910, 8, 12; van Suchtelen and Itano, *J. Amer. Chem. Soc.*, 1914, 36, 1793; Harned, *ibid.*, 1917, 39, 252; Freak, *J. Chem. Soc.*, 1919, 115, 55.

‡ Kolthoff, *Z. anal. Chem.*, 1922, 61, 171; Lucasse and Abrahams, *J. Chem. Ed.*, 1930, 7, 341.

After the end-point is reached the conductance increases due to the presence of barium hydroxide in solution. Harned utilized this method to titrate sulphates of magnesium, calcium, copper, nickel and cobalt.*

Empirical Determination of Basicity of an Acid—During the course of his studies on the conductance of solutions of sodium salts of various acids, Ostwald † discovered the empirical relation

$$\Lambda_{1024} - \Lambda_{32} = 10b,$$

where Λ_{1024} and Λ_{32} are the equivalent conductances at 25° of the salt at dilutions of 1024 and 32 litres, respectively, and b is the basicity of the acid. The results in Table XXI are taken from Ostwald's work and show that the relationship is approximately true.

TABLE XXI
EQUIVALENT CONDUCTANCES OF SODIUM SALTS OF ACIDS OF
DIFFERENT BASICITY

Sodium salt of :	Λ_{1024}	Λ_{32}	Difference.	Basicity.
Nicotinic acid	78.8	68.4	10.4	1
Quinolinic acid (1.2)	97.0	77.2	19.8	2
Pyridine tricarboxylic acid (1.2.4)	111.8	82.4	29.4	3
Pyridine tetracarboxylic acid (1.2.3.4)	121.2	80.8	40.4	4
Pyridine pentacarboxylic acid	127.8	77.7	50.1	5

This empirical formula may be utilized to determine the basicity of an acid; the values of Λ_{1024} and Λ_{32} are determined for the sodium salt, and the difference, divided by 10, gives an approximate value of the basicity. The method is not altogether satisfactory when applied to inorganic acids, but it has been used to confirm the dibasic nature of persulphuric acid.†

*For other aspects of conductometric titration see Thiel and Roemer, *Z. physikal. Chem.*, 1908, 63, 711; Dutoit, *J. Chim. phys.*, 1910, 8, 27; Edgar, *J. Amer. Chem. Soc.*, 1917, 39, 914; Harned and Laird, *ibid.*, 1918, 40, 1213; Hirsch, *Z. anal. Chem.*, 1926, 68, 160; the series of papers by Kolthoff in *Z. anorg. Chem.*, 1920, 111, 112, and in *Z. anal. Chem.*, 1922, 61; 1923, 62; and the later references given at the head of this section. Further details of the theory and practice of conductometric titrations, including descriptions of simplified experimental methods, are to be found in the literature cited.

† *Z. physikal. Chem.*, 1887, 1, 105; 1888, 2, 901.

‡ Ostwald expressed his conductances in terms of Siemens' units; if these are converted into reciprocal ohms the value of $\Lambda_{1024} - \Lambda_{32}$ becomes equal to $10.8b$. For a more general equation of the same type, see Bredig, *ibid.*, 1894, 13, 191.

Determination of Solubilities—If s is the solubility in gm. equiv. per litre of a sparingly soluble salt, then 1 gm. equiv. is present in $1/s$ litres, or $1000/s$ c.c. The solution is so dilute that if κ is its specific conductance $1000 \kappa/s$ may be taken as the equivalent conductance of the solute at infinite dilution, since $\Lambda = \kappa v$, where v is the volume in c.c. containing 1 gm. equiv. If the ion conductances of the constituents of the salt are known Λ_0 may be put equal to $1000 \kappa/s$, and so the value of s determined. A saturated solution of silver chloride had a specific conductance of 2.40×10^{-6} recip. ohms at 18° ; the specific conductance of the water used as solvent was 1.16×10^{-6} , hence the conductance (κ) due to the silver chloride alone was 1.24×10^{-6} . The value of Λ_0 for silver chloride is

$$\Lambda_{\text{Ag}} (= 53.8) + \Lambda_{\text{Cl}} (= 65.3) = 119.1; \text{ therefore,}$$

$$1000 \times 1.24 \times 10^{-6} / s = 119.1$$

and the solubility,

$$s = 1000 \times 1.24 \times 10^{-6} / 119.1 \\ = 1.04 \times 10^{-5} \text{ gm. equiv. per litre.}$$

The method has been used for determining the solubilities of various salts and oxides; in accurate work allowance is made for the incomplete dissociation of the dissolved substance in its saturated solution.*

* Holleman, *ibid.*, 1893, 12, 125; Kohlrausch *et al.*, *ibid.*, 1893, 12, 234; 1903, 44, 197; 1908, 64, 129; Hulett, *ibid.*, 1901, 37, 385; Böttger, 1903, 46, 521; Prud'homme, *J. Chim. physique*, 1911, 9, 517; see also Johnson and Hulett, *J. Amer. Chem. Soc.*, 1933, 55, 2258.

CHAPTER VI

EQUILIBRIA IN ELECTROLYTES

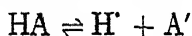
APPPLICATION of the Law of Mass Action—The degree of ionization of weak and intermediate electrolytes, at least, depends on the concentration of the solution, and there is presumably at every dilution an equilibrium between un-ionized molecules and ions. Thus for an electrolyte BA the equilibrium may be represented by



If the law of mass action † be applied, then

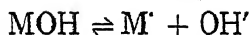
$$\frac{[B'] [A']}{[BA]} = \text{a constant, called the dissociation (or ionization)}$$

constant. Thus for a monobasic acid HA,



$$\text{and } k_a = \frac{[H'] [A']}{[HA]} ;$$

and for a base



$$\text{and } k_b = \frac{[M'] [OH']}{[MOH]} .$$

Consider a solution of concentration c gm. mol. per litre ; if the degree of ionization, or dissociation, at this concentration is α , then there are present $1 - \alpha$ gm. mol. of un-ionized molecules BA, and α gm. ions of B' and A' per litre. It follows that

$$[B'] = \alpha c ; [A'] = \alpha c \text{ and } [BA] = (1 - \alpha)c ;$$

$$\text{hence } \frac{\alpha c \times \alpha c}{(1 - \alpha)c} = \frac{\alpha^2 c}{1 - \alpha} = \text{dissociation constant } (k) . \quad (i)$$

* B' is used instead of B⁺ for the cation, and A' instead of A⁻ for the anion ; this type of symbol is used throughout the rest of the book.

† Square brackets are used to denote concentrations ; in electro-chemistry these are invariably expressed as gm. *mols.* or gm. *ions* per litre when applying the law of mass action. Strictly speaking, 'activities' (see p. 112) should be used instead of concentrations, but for the present, especially as far as weak electrolytes are concerned, the difference is of little consequence.

This equation gives the relationship between the degree of dissociation and the dilution, at a definite temperature; if the value of α is known for a certain value of the concentration c , then k may be calculated, and from it the degree of dissociation at any other concentration. The formula given here was first deduced by Ostwald; * it is the symbolic expression of what is known as Ostwald's Dilution Law. The derivation of the law depends, of course, on the applicability of the law of mass action to charged ions.

In the earlier attempts to verify equation (i) the value of α was taken to be equal to Λ/Λ_0 , that is the conductance ratio was assumed to be identical with the degree of dissociation: the dilution law equation can then be written in the form

$$k = \frac{\Lambda^2 c}{\Lambda_0(\Lambda_0 - \Lambda)} \quad \dots \dots \dots (ii)$$

In spite of the approximate nature of the equation it is in satisfactory agreement with conductivity measurements made with weak acids in bases: † the figures quoted in Table XXII indicate the type of results obtained with the simple equation (ii), and show the approximate constancy of the function k .

TABLE XXII
VERIFICATION OF OSTWALD'S DILUTION LAW

Dilution litres per gm. equiv.	Acetic Acid.	Λ $\Lambda_0 = 388$ (Kendall).	α	k
7.91	4.618	0.0119	1.81×10^{-4}
15.82	6.561	0.0169	1.84
31.63	9.260	0.0238	1.85
63.26	13.03	0.0336	1.85
126.52	18.30	0.0472	1.85
506.1	35.67	0.0920	1.84
1012.2	49.50	0.1276	1.84
Ammonium Hydroxide. $\Lambda_0 = 237$ (Bredig).				
8	3.20	0.0135	2.3×10^{-4}
16	4.45	0.0188	2.3
32	6.28	0.0265	2.3
64	8.90	0.0376	2.3
128	12.63	0.0533	2.3
256	17.88	0.0754	2.4

The dilution law has been considered to hold, for weak electrolytes, with an accuracy exceeding that usually found when the law

* *Z. physikal. Chem.*, 1888, 2, 36.

† Ostwald, *ibid.*, pp. 36, 270; 1889, 3, 170, 241, 369; Bredig, *ibid.*, 1894, 13, 289; Rivett and Sidgwick, *J. Chem. Soc.*, 1910, 97, 734; Kendall, *J. Amer. Chem. Soc.*, 1914, 30, 1069. Many other instances are to be found in the literature; see references on pp. 98, 385.

of mass action is applied to gaseous systems.* By applying corrections for the influence of concentration on the velocity of the ions in calculating the degree of dissociation (p. 79; see also p. 162), and by using the activity concept (p. 112), remarkably constant values of the 'dissociation constant' have been obtained.

The applicability of the dilution law may be tested by another method; equation (ii) may be written in the form

$$\Lambda c = k \frac{\Lambda_0^2}{\Lambda} - k \Lambda_0 \quad \text{. (iii)}$$

For a given electrolyte Λ_0 is a constant, and so

$$\Lambda c = \frac{a}{c} - b \quad \text{. (iv)}$$

where a and b are constants; if Λc is plotted against $1/\Lambda$, a straight line should, therefore, be obtained. Further, since Λ is equal to $1000\kappa/c$, the graph of κ , the specific conductance, against Λ should be a straight line. This has been verified for many aqueous and non-aqueous solutions. In general the dilution law is applicable to non-aqueous solvents, and attempts have been made to connect the dissociation constants of acids and bases in different solvents with certain physical properties, particularly the dielectric constant of the solvent.†

For a very weak electrolyte α is extremely small, and $1 - \alpha$ is practically equal to unity; the dilution law (equation i) may then be written in the approximate form:

$$k = \alpha^2 c$$

$$\text{or } \alpha = \sqrt{k/c} \quad \text{. (v)}$$

In a N -solution of any electrolyte, $c = 1$, and the degree of dissociation, α , is approximately equal to the square root of the dissociation constant. Another interpretation of this constant may be obtained by putting $\alpha = 0.5$, when equation (i) reduces to

$$k = \frac{(0.5)^2 c}{0.5} = 0.5c, \text{ or } c = 2k \quad \text{. (vi)}$$

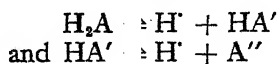
The concentration of an electrolyte at which it is half ionized is equal to twice the dissociation constant. For acetic acid k is

* Partington, *Trans. Faraday Soc.*, 1919, 15, 98.

† Baur, *Z. Elektrochem.*, 1905, 11, 931; Krüger, *ibid.*, 1911, 17, 453; Walden, *Z. physikal. Chem.*, 1920, 94, 263; Pring, *Trans. Faraday Soc.*, 1924, 19, 705; Bradley and Lewis (W. C. McC.), *J. Physical Chem.*, 1925, 29, 782; Hunt (H.) and Briscoe, *ibid.*, 1929, 33, 1495; Bjerrum, *Chem. Reviews*, 1928, 5, 231; Wynne-Jones, *Proc. Roy. Soc.*, 1933, 140 A, 440; Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, 55, 1019.

1.8×10^{-5} ; hence the acid is half ionized when a solution contains 3.6×10^{-5} gm. equiv. per litre.

Dibasic Acids—Since weak dibasic acids ionize in two stages, there are two dissociation constants:



$$k_1 = \frac{[\text{H}^+][\text{HA}']}{[\text{H}_2\text{A}]} \text{ and } k_2 = \frac{[\text{H}^+][\text{A}']}{[\text{HA}']}$$

At dilutions up to one or two thousand litres the second stage of ionization is practically negligible; the acid may then be treated as monobasic and the first stage dissociation constant (k_1) determined from conductance measurements.* When the second stage ionization becomes appreciable the variation of the conductance with dilution becomes complex; from the results it is possible, on the basis of certain approximations and assumptions, to calculate k_2 ,† but other more convenient methods based on the determination of hydrogen ion concentrations are available (p. 385).

In Table XXIII are given some of the approximate values for the dissociation constants of various acids and bases; in view of matters to be discussed later (p. 112) these quantities cannot be

TABLE XXIII

DISSOCIATION CONSTANTS OF WEAK ACIDS AND WEAK BASES (25°)

Acids.		Bases. k_b	
HF	6.9×10^{-4}	NH_3	1.8×10^{-2}
HCN	1.3×10^{-9}	CH_3NH_2	4.0×10^{-2}
HNO_2	4×10^{-4}	$(\text{CH}_3)_2\text{NH}$	5.0×10^{-2}
$\text{H}\cdot\text{COOH}$	2×10^{-4}	$(\text{CH}_3)_3\text{N}$	6.5×10^{-2}
$\text{CH}_3\cdot\text{COOH}$	1.8×10^{-5}	$\text{C}_2\text{H}_5\cdot\text{NH}_2$	4.6×10^{-2}
$\text{C}_2\text{H}_5\cdot\text{COOH}$	1.3×10^{-5}	$n\text{-C}_3\text{H}_7\cdot\text{NH}_2$	3.9×10^{-2}
$\text{CH}_2\text{Cl}\cdot\text{COOH}$	1.5×10^{-3}	$\text{C}_6\text{H}_5\cdot\text{NH}_2$	4×10^{-2}
$\text{C}_6\text{H}_5\cdot\text{COOH}$	6.1×10^{-4}	DIBASIC ACIDS. k_1 k_2	
$o\text{-C}_6\text{H}_4(\text{NO}_2)\text{COOH}$	6.4×10^{-3}	Oxalic acid $\times 10^{-2}$	3×10^{-2}
$m\text{-C}_6\text{H}_4(\text{NO}_2)\text{COOH}$	3.2×10^{-4}	Succinic acid 6.7×10^{-5}	6.0×10^{-2}
$p\text{-C}_6\text{H}_4(\text{NO}_2)\text{COOH}$	3.9×10^{-4}	Tartaric acid 9.6×10^{-4}	$\times 10^{-2}$
$\text{C}_6\text{H}_5\cdot\text{OH}$	1.0×10^{-10}	Maleic acid 1.1×10^{-2}	$\times 10^{-2}$

regarded as absolute constants. The values are changed if neutral electrolytes are added. The effect of temperature is indicated in Tables XXIIIA and XXIIIB.

* See, for example, Ives, Linstead and Riley, *J. Chem. Soc.*, 1932, 1093; Vogel (A. I.) *et al.*, *ibid.*, 1934, 21; 1935, 1624; MacInnes and Shedlovsky, *J. Amer. Chem. Soc.*, 1935, 57, 1705.

† Wegscheider, *Monatsh.*, 1902, 23, 635; 1912, 33, 899; 1916, 37, 251; *Z. Elektrochem.*, 1908, 14, 740; 1914, 20, 18; McCoy, *J. Amer. Chem. Soc.*, 1908, 30, 688; Chandler, *ibid.*, p. 694.

TABLE XXIII A

VARIATION WITH TEMPERATURE OF k_a FOR ACETIC ACID AND k_b FOR AMMONIUM HYDROXIDE

Temperature.	18°	100°	156°	218°	306°
$k_a(\text{CH}_3\text{COOH})$	1.72×10^{-5}	1.35×10^{-5}	6.28×10^{-6}	1.80×10^{-6}	9.3×10^{-7}
$k_b(\text{NH}_4\text{OH})$	1.83×10^{-5}	1.11×10^{-5}	5.36×10^{-6}	1.72×10^{-6}	1.39×10^{-7}

TABLE XXIII B

VARIATION OF DISSOCIATION CONSTANT OF ACETIC ACID FROM 0° TO 60°

Temperature.	0°	5°	15°	20°	25°	35°	40°	60°
$k_a \times 10^5$	1.657	1.700	1.745	1.753	1.754	1.728	1.703	1.542

The results in Table XXIII B, obtained by Harned and Ehlers,* using specially accurate methods, show that the dissociation constant of acetic acid has a maximum value at about 25°.[†]

Distribution of a Base between two Acids—The application of the law of mass action to mixtures of weak acids has given interesting results and some examples will now be considered. The arguments refer equally to weak bases, to which the simple form of the law of mass action is applicable. Suppose a_1 gm. equivs. of a weak acid HA_1 , a_2 gm. equivs. of another weak acid HA_2 , and b gm. equivs. of a strong base BOH are mixed in 1 litre of solution; if b is less than $a_1 + a_2$, then only a portion of each of the acids will be neutralized. Let x represent the fraction of each equivalent of base reacting with the acid HA_1 , then $1 - x$ will be the fraction reacting with HA_2 . Since k_1 and k_2 , the dissociation constants of HA_1 and HA_2 , may be represented by the equations

$$k_1 = \frac{[\text{H}^+][\text{A}_1']}{[\text{HA}_1]} \quad \text{and} \quad k_2 = \frac{[\text{H}^+][\text{A}_2']}{[\text{HA}_2]},$$

where $[\text{H}^+]$ is the hydrogen ion concentration in the final mixture, then

$$\frac{k_1}{k_2} = \frac{[\text{A}_1'] [\text{HA}_2]}{[\text{A}_2'] [\text{HA}_1]} \quad \dots \quad \text{(vii)}$$

If the solution under discussion is dilute the concentration of the anions A_1' and A_2' may be written as almost equal to the concentration of the salts BA_1 and BA_2 ; that is to bx and $b(1 - x)$ gm. ions per litre respectively. The concentration of each of the undissociated weak acids (HA_1 and HA_2) may be regarded as equal to its total concentration, that is to $a_1 - bx$, and $a_2 - b(1 - x)$ gm. mols. per litre respectively, since the degree of dissociation will be small; hence

$$\frac{k_1}{k_2} = \frac{bx\{a_2 - b(1 - x)\}}{b(1 - x)(a_1 - bx)} = \frac{x}{1 - x} \cdot \frac{\{a_2 - b(1 - x)\}}{a_1 - bx} \quad \dots \quad \text{(viii)}$$

* *J. Amer. Chem. Soc.*, 1933, 55, 652.

[†] This type of behaviour is quite general; for summary, see Harned. *ibid.*, 1934, 56, 1050.

If the ratio in which the base divides itself between the two acids can be determined experimentally, then the ratio of the dissociation constants may be calculated. The equation can be simplified by considering the special case in which equivalent amounts of each acid HA_1 and HA_2 are mixed with one equivalent of the strong base, that is by making the conditions such that $a_1 = a_2 = b$. The relationship then reduces to

$$\frac{1}{\sqrt{1 - \alpha}} \quad \dots \quad (ix)$$

Strengths of Acids—The hydrogen ion is generally accepted as the criterion of acidity (p. 179), and the strength of an acid is determined by the ease with which it can yield these ions. Since the dissociation constant of an acid HA may be regarded as being equal to the ratio of the velocity of dissociation into H^+ and A' ions to the velocity of their re-combination, it is evident that the dissociation constant is at least an approximate measure of the strength of an acid. The subject may be considered more explicitly in the following manner: if α is the degree of dissociation of an acid at a concentration of c , then the hydrogen ion concentration in this solution is αc gm. ions per litre. For two acids at the same total concentration, the ratio of the hydrogen ion concentrations will be α_1/α_2 ; substituting values for α obtained from equation (v), it follows that this ratio, and hence the ratio of the strengths of the two acids is $\sqrt{k_1/k_2}$. It has been seen in the previous section (equation ix) that when 1 gm. equiv. of a strong base is added to a solution containing 1 gm. equiv. of each of two acids, the base divides itself between the two acids in the ratio $\sqrt{k_1/k_2}$; this distribution, therefore, provides a method for comparing the strengths of acids.* The proportion of base which unites with each of the acids may be determined by thermal measurements,† by measuring volume changes, or by observing alterations in refractive index.‡ The results obtained, called the relative ‘avidities’ of acids, are probably only of qualitative interest, and their significance is doubtful for the strong acids studied.

Since the ratio of the hydrogen ion concentrations for two weak acids is α_1/α_2 , it is also possible to compare the strengths of such acids by means of conductance measurements. For a weak acid the degree of dissociation is given with fair accuracy by the conductance ratio, Λ/Λ_0 ; hence the ratio of the strengths of two acids is $\Lambda^I\Lambda_0^{II}/\Lambda_0^I\Lambda^{II}$, where Λ^I and Λ^{II} are measured at the same con-

* Cf. Arrhenius, *Z. physikal. Chem.*, 1890, 5, 14.

† Thomsen, *Ann. Physik*, 1854, 91, 83; 1869, 138, 65; *Phil. Mag.*, 1870, 39, 410.

‡ Ostwald, *J. prak. Chem.*, 1878, 18, 328.

centration for both acids. The ionic conductance of the hydrogen ion in aqueous solution is much greater than that of any anion with which it may be associated in an acid; therefore the equivalent conductances of all acids at infinite dilution are almost equal. The expression developed for the relative strengths of two acids can thus be reduced to the approximate form Λ^I/Λ^{II} . Although the conductance method has been used to compare the strengths of strong, highly ionized acids, the results probably have no significance since Λ/Λ_0 is no longer a measure of the degree of dissociation.

It has been known for some years that acids accelerate the rate of hydrolysis of esters and of cane sugar, and it was found that the catalytic influence of the acid was roughly proportional to its concentration; further Ostwald * observed that the rate of hydrolysis was greater for a strong acid than for a weak one. These results led Arrhenius † to the conclusion that the catalytic effect of an acid was proportional to its hydrogen ion concentration, and so to its strength at a given total concentration; this author used Ostwald's measurements on the rate of inversion of cane sugar, and of ester hydrolysis in the presence of various acids, to compare their strengths. It is now generally agreed, ‡ however, that in addition to hydrogen ions, undissociated molecules of the acid and the anions can be catalytically active, so that the results can only be regarded as approximate. The strengths of bases have been determined by procedures exactly analogous to those described above.

The most reliable methods for comparing the strengths of acids are those based on direct determination of the dissociation constants, either from conductance measurements or from the *E.M.F.*'s of suitable cells. Hydrogen ion concentrations may also be compared by means of indicators (p. 252) or by *E.M.F.* methods (Chap. XV).

Mutual Effect of Ions—Returning to a consideration of the law of mass action, it will now be shown how it may be used to give information concerning the mutual influence of ions in a mixture of electrolytes. Consider the effect of adding a weak acid HA_I to a solution of another, HA_{II} ; suppose c_1 and c_2 are the total concentrations of the respective acids in the mixture, β_1 and β_2 the degrees of dissociation, and k_1 and k_2 the dissociation constants. The concentration of the hydrogen ions may be written as $\beta_1 c_1 + \beta_2 c_2$, and of the A_I' and A_{II}' ions as $\beta_1 c_1$ and $\beta_2 c_2$, respectively; the concentrations of the undissociated acids may be taken as $(1 - \beta_1)c_1$

* *Ibid.*, 1883, 27, 1.

† *Z. physikal. Chem.*, 1890, 5, 1.

‡ For summary of evidence, see Glasstone, *Recent Advances in General Chemistry*, 1936, Chap. VIII.

and $(1 - \beta_2)c_2$. Applying the law of mass action to each acid separately, it is found that

$$k_1 = \frac{(\beta_1 c_1 + \beta_2 c_2)(\beta_1 c_1)}{(1 - \beta_1)c_1} \text{ and } k_2 = \frac{(\beta_1 c_1 + \beta_2 c_2)(\beta_2 c_2)}{(1 - \beta_2)c_2}$$

$$\therefore \frac{k_1}{k_2} = \frac{\beta_1(1 - \beta_2)}{\beta_2(1 - \beta_1)} \quad \dots \quad (x)$$

Since both acids are weak β_1 and β_2 will be small; hence $1 - \beta_1$ and $1 - \beta_2$ may be regarded as equal, and it follows that

$$\frac{k_1}{k_2} = \frac{\beta_1}{\beta_2} \quad \dots \quad (xi)$$

The degree of dissociation of each acid in a mixture of two acids is thus proportional to its dissociation constant, and the stronger acid will be dissociated to the greater extent. The degree of dissociation in the mixture is not, however, the same as in a solution of a single acid at the same concentration; let α_1 and α_2 be the degrees of dissociation in separate solutions of HA_I and HA_{II} at concentrations c_1 and c_2 , respectively. Then as a first approximation

$$k_1 = \alpha_1^2 c_1 \text{ and } k_2 = \alpha_2^2 c_2 \quad \dots \quad (xii)$$

(see equation v); in the mixture, however, taking $1 - \beta_1 \approx 1$,

$$k_1 = (\beta_1 c_1 + \beta_2 c_2)\beta_1 \quad \dots \quad (xiii)$$

Dividing both sides of equation (xiii) by β_1^2 , there results

$$\frac{k_1}{\beta_1^2} = c_1 + \frac{\beta_2 c_2}{\beta_1} \quad \dots \quad (xiv)$$

Since $\beta_2/\beta_1 = k_2/k_1$ (equation xi), and $k_1 = \alpha_1^2 c_1$ (equation xii), then

$$\frac{\alpha_1^2 c_1}{\beta_1^2} = c_1 + \frac{k_2 c_2}{k_1} \quad \dots \quad (xv)$$

$$\therefore \frac{\alpha_1}{\beta_1} = \sqrt{1 + \frac{k_2 c_2}{k_1 c_1}} \quad \dots \quad (xiv)$$

In the same way it may be shown that

$$\frac{\alpha_2}{\beta_2} = \sqrt{1 + \frac{k_1 c_1}{k_2 c_2}} \quad \dots \quad (xvii)$$

These expressions permit the determination of the change in dissociation of an acid when mixed with another acid. A good qualitative idea of the mutual influence of two acids may be obtained by considering the case in which k_1/k_2 is, say, 15, i.e. HA_I is stronger than HA_{II} , and c_1 and c_2 are both 1 gm. equiv. per litre. In these circumstances α_1/β_1 is approximately unity, whereas α_2/β_2 is equal to 4; hence the dissociation of the stronger acid is hardly affected, but that of the weaker acid is much reduced.

Water Correction in Conductance of Weak Acids—A special case of the mutual influence of two acids is encountered in the determination of the conductance of a weak acid. The main conducting impurity in conductivity water in contact with air is probably carbonic acid, resulting from an equilibrium with carbon dioxide in the atmosphere (see p. 64). If a weak acid is dissolved in this water the ionization of both acids will be repressed so that the measured conductance is less than the sum of the two separate conductances; it is not satisfactory, therefore, to subtract from the conductance of the solution that of the original water in order to obtain the value for the added acid. The method of calculating the correction* is as follows. Let κ be the measured specific conductance of the solution containing c gm. equivs. per litre of a weak acid HA; then the apparent equivalent conductance, Λ , of the acid will be $1000\kappa/c$, although this is actually due both to the solute and to carbonic acid. Since the equivalent conductance at infinite dilution for all weak acids is about the same (p. 101), the apparent conductance ratio of the acid will be given by

$$\alpha = \frac{\Lambda}{\Lambda_0} = \frac{1000\kappa}{c\Lambda_0} \quad (\text{xviii})$$

and

$$\kappa = \alpha c \Lambda_0 / 1000 \quad (\text{xix})$$

where Λ_0 may be taken as the value for the acid under examination. Since both carbonic acid and the acid HA yield hydrogen ions, the concentration of these will be αc , i.e. $1000\kappa/\Lambda_0 = h$, say, gm. ions per litre. Carbonic acid, being a weak acid, will ionize almost entirely in its monobasic form, thus $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3'$, and the dissociation constant will be given approximately by

$$k = \frac{[\text{H}^+][\text{HCO}_3']}{[\text{H}_2\text{CO}_3]} \quad (\text{xx})$$

which is known to be 4.5×10^{-7} at 25° . The concentration of H_2CO_3 may be taken as equal to the solubility of carbon dioxide in conductivity water when in equilibrium with air, i.e. 1.4×10^{-5} gm. mols. per litre; therefore,

$$[\text{HCO}_3'] = \frac{k[\text{H}_2\text{CO}_3]}{[\text{H}^+]} = \frac{4.5 \times 10^{-7} \times 1.4 \times 10^{-5}}{h} = \frac{6.3 \times 10^{-12}}{h} = b \quad (\text{xxi})$$

The ionization of carbonic acid must have produced an equivalent amount of hydrogen ions; hence the concentration of the latter due to HA must be $h - b$, and this must also equal the concentration of A' ions produced by this acid. As the carbonic acid has

* Walker and Cormack, *J. Chem. Soc.*, 1900, 77, 5; Kendall, *J. Amer. Chem. Soc.*, 1917, 39, 7; see, however, Washburn, *ibid.*, 1918, 40, 109.

depressed the ionization of HA, these values do not represent its true ionization at the concentration c ; the theoretical value in the absence of carbonic acid may, however, be calculated. Since HA is a weak acid, and only slightly ionized under any circumstances, the concentration of un-ionized acid, i.e. $[HA]$, is almost constant at a given total concentration; hence $[H^+][A^-]$ may be regarded as constant, whether carbonic acid is present or not. Under all conditions, therefore, for an acid concentration c ,

$$[H^+][A^-] = h(h - b) = \text{constant} \quad \dots \quad (\text{xxii})$$

For the pure acid $[H^+] = [A^-]$, and so each must be equal to $\sqrt{h(h - b)}$; the true degree of ionization of the pure acid is then $\sqrt{h(h - b)}/c$. The specific conductance may in general be written as $\kappa\Lambda_0/1000$ (equation xix), hence the *corrected* specific conductance of the acid HA at the concentration c is equal to

$$\Lambda_0\sqrt{h(h - b)}/1000.$$

In a particular case, when the acid HA was phenol, the value of κ measured at 25° for a 0.1240 molar solution was 1.60×10^{-6} recip. ohms; the equivalent conductance at infinite dilution, determined from measurements on sodium phenoxide and from the known mobility of the hydrogen ion, is 380 recip. ohms. Substituting these values it is found that h is 43×10^{-7} and b is 14.6×10^{-7} gm. ions per litre. Hence the corrected specific conductance of the phenol is 1.33×10^{-6} recip. ohms.

It may be shown that for acids stronger than acetic acid, that is when the dissociation constant is greater than 10^{-5} , the carbonic acid correction is negligible. The acid HA is then much the stronger and so depresses the ionization of the carbonic acid to such an extent that the latter contributes almost nothing to the conductance. For acids weaker than acetic the correction, however, becomes appreciable; the weaker the acid the greater the correction.

Mixture of Strong and Weak Electrolyte—The effect on a weak acid of a strong acid, e.g. hydrochloric acid, cannot be derived from the formulæ given above, since the law of mass action in its simple form does not apply to the latter (*vide infra*). An alternative treatment can, however, be used: if c_1 and c_2 are the concentrations of the weak and strong acid, and β_1 and β_2 the degrees of dissociation, respectively, in the mixture, then for the weak acid

$$k_1 = (\beta_1 c_1 + \beta_2 c_2)\beta_1,$$

(see equation xiii), since β_1 is small and $1 - \beta_1 \approx 1$. For the strong acid β_2 is large and may be taken as unity; the equation then reduces to

$$k_1 = (\beta_1 c_1 + c_2)\beta_1 = \beta_1^2 c_1 + \beta_1 c_2 \quad \dots \quad (\text{xxiii})$$

Since β_1 is a small fraction, β_1^2 is negligibly small, and so

$$k_1 = \beta_1 c_2$$

and

$$\beta_1 = k_1/c_s \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{xxiv})$$

The degree of ionization of a weak acid in a mixture with a strong acid is, therefore, inversely proportional to the concentration of the latter; by adding a large quantity of a strong acid the ionization of a weak acid may be reduced to a very small amount. This behaviour is an example of a general phenomenon, namely the decrease in ionization of an electrolyte as a consequence of the addition of an ion already present in solution. For any weak electrolyte AB,



and

$$k = \frac{[A'] [B']}{[AB]}.$$

If to the solution there is added a strong electrolyte which yields a large concentration of the ion A' , then in order to maintain the equilibrium constant of AB the concentration of B' ions must decrease or of undissociated AB increase, or both. In general a certain proportion of A' and B' ions unite to form undissociated AB , and so the degree of dissociation of the latter is decreased by the addition of a common ion. The ionization of a weak acid, therefore, is reduced in the presence of one of its salts, which supplies the common anions, or of a strong acid, which yields hydrogen ions. Similarly, the degree of dissociation of a weak base is decreased by the addition of either one of its salts or a strong base; the former produces a large excess of cations, and the latter of hydroxyl ions.

From a knowledge of the dissociation constant of a weak acid it is possible to calculate approximately the hydrogen ion concentration in the presence of a salt, by means of an equation similar to (xxiv), viz.

$$\beta = k/c,$$

where β is the degree of dissociation of the acid in the presence of a concentration c_2 of salt. If c_1 is the total concentration of the acid then the hydrogen ion concentration is given approximately by βc_1 .* Calculations of this type were made by Arrhenius† for mixtures of acetic acid and sodium acetate, and of formic acid and sodium formate; the results were in good agreement with the values for the hydrogen ion concentrations determined from the catalytic influence of the various mixtures on the inversion of cane sugar. In view of the fact that no allowance was made for the

* For more complete treatment, see Chap. IX.

† *Z. physikal. Chem.*, 1889, 4, 226; 1890, 5, 7.

catalytic activity of either un-ionized molecules of acid or of the anions, the excellent agreement may be due, to some extent at least, to the balancing of errors. The general conclusions concerning the influence of a common ion are, however, amply confirmed.

Common Ion Effect—The decrease in ionization resulting from the addition of a common ion plays an important rôle in analytical chemistry. In a strongly acid solution of hydrogen sulphide, for example, the ionization of the latter is so greatly repressed by the hydrogen ions as to reduce the concentration of S^{2-} ions to such an extent that the solubility product of nickel and cobalt sulphides is not exceeded; these sulphides cannot, therefore, be precipitated in a strongly acid medium. In the presence of acetic acid, however, the ionization of the hydrogen sulphide is reduced only slightly, and sufficient sulphide ions are present to allow cobalt and nickel sulphides to be precipitated. Another instance of the same type is the repression of the ionization of ammonium hydroxide, and the reduction in hydroxyl ion concentration as a consequence of the addition of ammonium chloride. The hydroxyl ion concentration may be made low enough in this way to prevent the precipitation, for example, of magnesium hydroxide; ferric, aluminium and chromic hydroxides are precipitated, however, because of their very small solubility products.

Isohydric Solutions—The addition of a common ion generally reduces the dissociation of an electrolyte, yet it is possible to mix two solutions of different electrolytes containing a common ion without the dissociation of either being affected. This only occurs in certain circumstances, and is partly a consequence of the fact that the actual concentration of each electrolyte is reduced when the two separate solutions are mixed. Solutions of acids which do not change their ionization on mixing are said to be **isohydric** with one another; the conditions for isohydry may be deduced in the following manner.* Consider solutions of two weak acids HA_I and HA_{II} present at concentrations of c_1 and c_2 gm. mols. per litre, respectively, before mixing; if α_1 and α_2 are the degrees of dissociation, and k_1 and k_2 the dissociation constants, then by the dilution law,

$$k_1 = \frac{\alpha_1^2 c_1}{1 - \alpha_1} \quad \text{and} \quad k_2 = \frac{\alpha_2^2 c_2}{1 - \alpha_2} \quad \dots \quad (\text{xxv})$$

Suppose v_1 litres of the first acid solution are mixed with v_2 litres of the second, then if the degrees of dissociation remain unchanged, it follows that in the mixture

$$[H^+] = \frac{\alpha_1 c_1 v_1 + \alpha_2 c_2 v_2}{v_1 + v_2} \quad \dots \quad (\text{xxvi})$$

* Arrhenius, *ibid.*, 1888, 2, 284.

since both acids yield hydrogen ions. The concentrations of anions and of undissociated molecules of the acid HA_I are given by

$$[A_I] = \frac{\alpha_1 c_1 v_1}{v_1 + v_2} \quad \text{and} \quad [\text{HA}_I] = \frac{(1 - \alpha_1) c_1 v_1}{v_1 + v_2} \quad (\text{xxvii})$$

and so,

$$k_1 = \frac{(\alpha_1 c_1 v_1 + \alpha_2 c_2 v_2) \alpha_1}{(1 - \alpha_1)(v_1 + v_2)} \quad \dots \quad (\text{xxviii})$$

Comparing equations (xxv) and (xxviii), it is found that

$$\alpha_1 c_1 v_1 + \alpha_2 c_2 v_2 = \alpha_1 c_1 (v_1 + v_2) \quad \dots \quad (\text{xxix})$$

By considering the dissociation constant (k_2) of the acid HA_{II} , the analogous result

$$\alpha_1 c_1 v_1 + \alpha_2 c_2 v_2 = \alpha_2 c_2 (v_1 + v_2) \quad \dots \quad (\text{xxx})$$

is obtained: from these two equations it follows that

$$\alpha_1 c_1 = \alpha_2 c_2 \quad \dots \quad (\text{xxxi})$$

Now $\alpha_1 c_1$ is the concentration of hydrogen ions in the original solution of the acid HA_I , and $\alpha_2 c_2$ the value for the solution of HA_{II} before mixing; hence it is seen that two solutions of a weak electrolyte are isohydric when they contain the common ion, in this case the hydrogen ion, at the same concentration. In general the term **iso-ionic** may be used for solutions which do not alter their ionization on mixing.

The Conductance of Mixtures *—When two iso-ionic solutions are mixed the conducting power of the mixture is the sum of the conducting powers of the separate solutions, since there is no change in the number of each ionic species on mixing; it is thus possible to calculate the conductance of the mixed solution. Let κ_1 and κ_2 be the specific conductances of two iso-ionic solutions, of which volumes v_1 and v_2 c.c., respectively, are mixed. The specific conductance is a measure of the conducting power of the ions in 1 c.c.; hence the conducting powers of the solutions before mixing are $\kappa_1 v_1$ and $\kappa_2 v_2$ respectively, and that of the mixture must be the sum of these, $\kappa_1 v_1 + \kappa_2 v_2$. The volume of the mixture is $v_1 + v_2$, assuming no expansion or contraction, and so its specific conductance κ_m is given by

$$\kappa_m = \frac{\kappa_1 v_1 + \kappa_2 v_2}{v_1 + v_2}$$

Any mixture of two electrolytes with a common ion may be considered as made up of two iso-ionic solutions, and the con-

* In the deductions made in this section it is assumed that the mobilities of the ions do not change either on dilution, or on mixing with another electrolyte. This is only approximately justifiable for weak electrolytes, but cannot apply to strong electrolytes as will be seen in the following chapter.

ductance calculated. Suppose the mixture contains c_1 and c_2 gm. mols. of two electrolytes per litre, and α_1 and α_2 are the degrees of dissociation in the mixture; the ionic concentrations due to the constituents separately will be $\alpha_1 c_1$ and $\alpha_2 c_2$ gm. ions per litre respectively. The total concentration of the common ion will be the sum of these, viz. $\alpha_1 c_1 + \alpha_2 c_2$ gm. ions per litre. Imagine the solution divided into two parts each of which contains only one electrolyte, and the volumes are $\alpha_1 c_1 / (\alpha_1 c_1 + \alpha_2 c_2)$ and $\alpha_2 c_2 / (\alpha_1 c_1 + \alpha_2 c_2)$ litres, respectively; the concentration of the common ion would then be $\alpha_1 c_1 + \alpha_2 c_2$ gm. ions per litre in each solution, and this is the same as its value in the mixture. The two solutions would then be iso-ionic, and the specific conductance of the mixture can be calculated from a knowledge of the specific conductances of the separate electrolytes, when each has an ionic concentration equal to the total concentration of the common ion in the mixture. In other words, in a solution containing two electrolytes, to which the iso-ionic principle is applicable, each electrolyte has a degree of dissociation equal to that it would have if present alone in a solution in which each of its ions has a concentration equivalent to that of the common ion in the mixture.* This idea has proved very useful in calculating the conductances of mixtures, provided the conductance of each constituent is known at various concentrations.

Schlesinger and Reed's Method—An interesting method for calculating the conductance of a mixture of two weak electrolytes with a common ion has been described by Schlesinger and Reed;† this method does not require a detailed knowledge of conductances at various ionic concentrations, but the dissociation constants and the equivalent conductances at infinite dilution of the constituents of the mixture must be known. Let c_1 and c_2 be the concentrations of the two weak electrolytes, and their dissociation constants k_1 and k_2 ; α_1 and α_2 are the respective degrees of dissociation in the mixture, then

$$k_1 = \frac{\alpha_1(\alpha_1 c_1 + \alpha_2 c_2)}{1 - \alpha_1} \quad \text{. (xxxii)}$$

and
$$k_2 = \frac{\alpha_2(\alpha_1 c_1 + \alpha_2 c_2)}{1 - \alpha_2} \quad \text{. . . (xxxiii)}$$

$$\alpha_1 = \frac{\alpha_2 k_1 / k_2}{1 - \alpha_2 (1 - k_1 / k_2)} \quad \text{. . . (xxxiv)}$$

Equation (xxxiii) may be written in the form

$$\alpha_1 c_1 + \alpha_2 c_2 = k_2 (1 - \alpha_2) / \alpha_2 \quad \text{. . . (xxxv)}$$

* Suggested empirically by Arrhenius, *Z. physikal. Chem.*, 1899, **31**, 218; see Noyes, *Technology Quarterly*, 1904, **17**, 301; *Science*, 1904, **20**, 577.

† *J. Amer. Chem. Soc.*, 1919, **41**, 1924.

and on dividing through by α_2 , this yields

$$c_1\alpha_1/\alpha_2 + c_2 = k_2(1 - \alpha_2)/\alpha_2^2 \quad . \quad . \quad . \quad (xxxvi)$$

If c_S is the concentration of the second electrolyte, in a solution containing that substance only, in which the degree of dissociation is equal to its value (α_2) in the mixture, then

$$k_2 = \frac{\alpha_2^2 c_S}{1 - \alpha_2} \text{ or } c_S = k_2(1 - \alpha_2)/\alpha_2^2 \quad . \quad . \quad (xxxvii)$$

Therefore, substituting in equation (xxxvi) it follows that

$$c_1\alpha_1/\alpha_2 + c_2 = c_S \quad . \quad . \quad . \quad (xxxviii)$$

For a series of arbitrarily chosen values of α_2 the corresponding values of α_1 and c_S may be calculated by means of equations (xxxiv) and (xxxvii), since k_1 and k_2 are known; α_1/α_2 can then be plotted against c_S or α_2 . The first step in the calculation is to choose a value of c_S which might be of the correct order of magnitude and then to read off the corresponding value of α_1/α_2 from the graph; by means of equation (xxxviii), c_S may be checked against the chosen value. If the results do not agree, another value of c_S is chosen, and the method of trial and error followed until agreement is obtained. It has been found that, in general, the conductances of mixtures of formates in formic acid may be quite accurately calculated by this method.*

It is interesting to note that equation (xxxviii) may be written in the form

$$\alpha_1 c_1 + \alpha_2 c_2 = \alpha_2 c_S.$$

Now $\alpha_1 c_1 + \alpha_2 c_2$ is the total concentration of the common ion in the mixture, and $\alpha_2 c_S$ is the ionic concentration in a solution of one of the components only in which the degree of dissociation, α_2 , is the same as in the mixture; hence it follows that the dissociation of each component of a mixture is the same as it would be when present alone in a solution of ionic concentration equal to that of the common ion in the mixture. This is identical with the deduction made on the basis of the iso-ionic principle, and so the two methods are fundamentally the same.

Mixtures of Strong Electrolytes—Although the iso-ionic principle should apply only to mixtures of weak electrolytes, for which the simple form of the dilution law holds, it has been found to represent quite accurately the conductance of a mixture of a weak and a strong acid.† It has been claimed that the principle is applicable to mixtures of strong electrolytes, and in fact some

* Solutions of formates in formic acid obey the Ostwald dilution law, taking α as the conductance ratio; Schlesinger *et al.*, *J. Amer. Chem. Soc.*, 1911, 33, 1924; 1914, 36, 1589; 1916, 38, 271; 1919, 41, 72.

† Arrhenius, *loc. cit.*; Wakeman, *Z. physikal. Chem.*, 1894, 15, 159.

authors have attributed deviations in the actual conductances from the calculated values to the formation of complex ions.* It is certain, however, that for strong electrolytes the iso-ionic principle cannot be adequate.† Barmwater ‡ has suggested a modified principle, according to which each electrolyte in a mixture with a common ion is assumed to be 'dissociated' to the same extent (i.e. it has the same conductance ratio) as if present alone in a solution at a concentration equal to the sum of the concentrations of the two electrolytes; that is, the equivalent conductance of each electrolyte in the mixture is equal to that for the pure salt when present alone at the same *total* concentration. A further modification, originally applied by Van Rysselberghe§ in connection with transport numbers, has been extended to the conductance of mixtures, with special reference to the alkali halides: || the fundamental assumption is that in any mixture of these salts the mobilities of the various ions are proportional to their values in solutions of the two salts alone at the same concentration as the total concentration of the mixture. The conductances calculated in this way are in better agreement with experiment than those based on the Barmwater principle in the more concentrated solutions: in dilute solutions both methods give similar results. Kraus** has expressed the view that the conductance ratio of a salt in a mixture depends on the *product* of the concentrations of the constituent ions, rather than on their sum: the conductances evaluated on this basis are in better harmony with the experimental data than are those based on the iso-ionic principle. The conductance of a mixture of strong electrolytes without an ion in common is apparently a function of the total concentration of electrolyte,†† but the conditions are here too complex for any simple rule to apply. It may be mentioned that modern views of electrical conduction, based on the concept of almost complete ionization of strong electrolytes coupled with inter-ionic attractions to account for the departure from ideal behaviour (see Chapter VII), require the mobility of an ion to depend on the 'ionic strength' (p. 116) of the solution, that is on the electrical environment of the ion.

* Hofmann, *ibid.*, 1903, 45, 584; Stearn, *J. Amer. Chem. Soc.*, 1922, 44, 670.

† Mackay, *ibid.*, 1911, 33, 308; Bray and Hunt, *ibid.*, p. 781; Loomis, Essex and Meacham, *ibid.*, 1917, 39, 1133.

‡ *Z. physikal. Chem.*, 1899, 28, 424; 1903, 45, 557; 1906, 56, 225; see also, Bray and Hunt, *loc. cit.*; Ruby and Kawai, *J. Amer. Chem. Soc.*, 1926, 48, 1119; Partington and King, *Trans. Faraday Soc.*, 1927, 23, 522; Garb and Hlasko, *Rocz. Chem.*, 1930, 10, 248.

§ *J. Amer. Chem. Soc.*, 1933, 55, 990.

|| Van Rysselberghe and Nutting, *ibid.*, 1934, 56, 1435.

** *Ibid.*, 1921, 43, 2507; *Electrically Conducting Systems*, 1922, p. 222.

†† See, for example, Sherrill, *ibid.*, 1910, 32, 741.

The Law of Mass Action and Strong Electrolytes—When applied to concentrated solutions of weak electrolytes, or to strong electrolytes at any dilution, except perhaps the very highest, the law of mass action, as already indicated, fails to hold. The results in Table XXIV for potassium chloride solutions show that the simple form of the dilution law breaks down completely; similar results are obtained for other strong electrolytes.

TABLE XXIV

APPLICATION OF THE LAW OF MASS ACTION TO A STRONG ELECTROLYTE
(POTASSIUM CHLORIDE AT 18°, $\Lambda_0 = 129.9$)

Litres per gm. equiv.	Λ	α	k
10	112.0	0.862	0.541
20	115.8	0.891	0.364
50	120.0	0.923	0.222
100	122.4	0.942	0.154
200	124.4	0.958	0.108
500	126.3	0.972	0.0681
1000	127.3	0.980	0.0485
2000	128.1	0.986	0.0352
5000	128.8	0.991	0.0223

In between weak electrolytes, e.g. acetic acid, and strong electrolytes, e.g. potassium chloride and other salts, there are intermediate substances, e.g. dichloroacetic acid; this type of electrolyte obeys the law of mass action in dilute solution, but at concentrations greater than about 1 gm. equiv. in 100 litres divergences occur. Many of these substances, as well as others which do not conform with the dilution law in aqueous solutions, do so in non-aqueous media.*

Various formulæ have been suggested from time to time to connect the degree of dissociation, or more correctly the conductance ratio, of strong electrolytes with the dilution; most of these are purely empirical and have no theoretical basis.† A modified form of the equation originally suggested by Storch‡ has been used by Kraus and Bray,§ and is supposed to represent the behaviour of many strong electrolytes, especially in non-aqueous solvents. The equation has the form:

$$\frac{\alpha^2 c}{1 - \alpha} = k_x (\alpha c)^m + k_y \quad (\text{xxxix})$$

* See Walden, *Elektrochemie nichtwässriger Lösungen*, 1924, p. 356 *et seq.*; Z. physikal. Chem., 1930, 148, 45.

† Rudolphi, Z. physikal. Chem., 1895, 17, 385; van 't Hoff, *ibid.*, 1895, 18, 300; Storch, *ibid.*, 1896, 19, 13; Kendall, J. Chem. Soc., 1912, 101, 1275; for summary, see Taylor, *Physical Chemistry*, 1931, p. 657 (Partington).

‡ See Falk and Noyes, J. Amer. Chem. Soc., 1912, 34, 454; Macdougall (F. H.), *ibid.*, p. 855.

§ *Ibid.*, 1913, 35, 1315.

and is equivalent to the Ostwald expression at high dilutions, when αc is negligible; this was designed to fit the supposed agreement of strong electrolytes with the law in very dilute solutions. In addition to the purely empirical equations others of a semi-theoretical nature have been proposed,* but recent developments in the theory of strong electrolytes (Chapter VII) make them unnecessary and they must be considered as mainly of historical interest.

Corrected Degree of Dissociation—In considering the causes of the deviation of strong electrolytes from the dilution law two important points must be mentioned. In the first place the conductance ratio may not be equal to the degree of dissociation, on account of variation of the speeds of the ions at different concentrations.† Using the correction described previously (p. 79; see also p. 162) it is probable that a closer approximation to the true degree of dissociation may be obtained from conductance measurements for weak or intermediate electrolytes. These corrections are not always sufficient, however, to eliminate divergences from the dilution law, especially for strong electrolytes.

The second factor to be considered is that even if the true degree of dissociation were known the concentrations determined in this manner may not necessarily represent the 'active masses' as required by the law of mass action. This point was realized several years ago ‡ and formulæ were suggested to allow for the reduction in the effective concentrations resulting from interactions between the ions themselves, and between ions and molecules. The equations involved a number of indeterminate coefficients and so did not meet with any success. Subsequently Lewis § introduced the concept of activity, which may be regarded crudely as the quantity to be substituted for the ordinary concentration in order to make the law of mass action applicable.

If ΔG represents the change of free energy when one gm. mol. or one gm. ion is transferred from a solution in which its molar fraction is N_1 to one in which its molar fraction is N_2 , then the corresponding activities may be defined by the relationship

$$-\Delta G = RT \ln a_1/a_2.$$

* For review and discussion, see Taylor, *Physical Chemistry*, 1931, p. 657 (Partington).

† Cf. Jahn, *Z. physikal. Chem.*, 1900, **33**, 545; Lewis, *J. Amer. Chem. Soc.*, 1912, **34**, 1631; MacInnes, *ibid.*, 1921, **43**, 1217; see especially, Chapter VII.

‡ See Jahn, *Z. physikal. Chem.*, 1900, **35**, 345; 1901, **37**, 490; Nernst, *ibid.*, 1901, **38**, 125, 457; Goebel, *ibid.*, 1902, **42**, 59.

§ *Ibid.*, 1908, **61**, 129.

|| It is becoming the practice to use G for the free energy instead of F which has been hitherto generally employed.

For an ideal solution, assuming Raoult's law, it can be shown that

$$- \Delta G = RT \ln N_1/N_2,$$

and so the ratio of activities represents the ratio of the *ideal* concentrations, and these would of necessity, according to thermodynamics, satisfy the law of mass action.

Activities were at first only determinable by purely empirical methods; hence they appeared to have no special value. In recent years, however, it has been found possible to calculate activities, at least in dilute solutions, on purely theoretical grounds, and so these quantities are beginning to acquire a definite physical significance (see Debye-Hückel theory, Chap. VII). It is true that in many instances the activity is used as an empirical device to overcome discrepancies between the actual and ideal behaviour of electrolytes, but it is one of the aims of physical chemistry to be able to calculate the activity of any ionic species from its known properties. There is no doubt that the introduction of the activity concept into electrochemistry has been justified, and use will be made of the idea throughout this book; it is important, however, to realize its limitations from the outset.

In very dilute solutions of strong electrolytes the activities of the ions are not very different from the concentrations calculated on the basis of the conductance ratio; hence it is found that such solutions appear to obey the law of mass action* in the form generally applied to weak electrolytes. The activity concept has been recently applied to weak, intermediate, and even to relatively strong, electrolytes, and it has been found that after making the appropriate correction the law of mass action is applicable in all cases to the equilibrium between ions and 'undissociated' molecules; the significance of the latter term is, however, extended (see p. 155).

The Activity Concept—Since activities have been defined in terms of a ratio, numerical values can only be obtained with reference to a standard state; the actual standard chosen may vary in different instances, but in electrochemistry the activity of a solute at infinite dilution is invariably defined as equal to its concentration. The concentration may be expressed in terms of molality (*m*), defined as the number of gm. mols. of solute per 1,000 gms. of solvent, or of volume concentration (*c*), i.e. gm. mols. per litre, or of the molar fraction, i.e. number of gm. mols. of solute divided by the total number of solute and solvent.† Although activity (*a*) and

* Arrhenius, *J. Chem. Soc.*, 1914, 105, 1414; Washburn, *J. Amer. Chem. Soc.*, 1918, 40, 150.

† According to Macfarlane and Gatty, *Phil. Mag.*, 1932, 13, 283, 291, the concentrations for electrochemical work should be expressed in terms of gm. mols. in a given volume of solvent.

concentration are regarded as equal at infinite dilution, the values are generally not equal at other concentrations. The fraction a/m (or a/c) is called the **activity coefficient** of the solute; it may be regarded as a measure of the extent to which an ion or molecule departs from ideal behaviour, since a represents the 'ideal' concentration, or active mass, and m (or c) the real concentration. In the thermodynamic treatment of activity coefficients developed by Lewis and Randall * the concentration of any particular ionic species is taken as the *total* possible molality (i.e. stoichiometric concentration) without any allowance being made for incomplete dissociation of the electrolyte. This (stoichiometric) activity coefficient is generally represented by the symbol γ ; it includes a factor for any deviation from complete ionization. For a given solution the value of the activity coefficient will depend on the method adopted for expressing concentrations; the differences, which are in any case small, are negligible in dilute solutions.

For a uni-univalent electrolyte, e.g. potassium chloride, of the general formula BA, there is an equilibrium; $BA \rightleftharpoons B^+ + A^-$, and if a_+ and a_- are the activities of the cations (B^+) and anions (A^-) respectively, whereas a_2 is the activity of the un-ionized or undissociated molecules, then

$$\frac{a_+ a_-}{a_2} = k \quad (xi)$$

Since the activities must comply with the law of mass action this equation is strictly accurate for all classes of electrolytes. The mean activity of the two ions, a_{\pm} , is regarded as the geometric mean of the separate activities, thus

$$a_{\pm} = \sqrt{a_+ a_-} = \sqrt{k a_2} \quad (xli)$$

The activity coefficients of the separate ions may be taken as a_+/m_+ and a_-/m_- respectively, where m_+ and m_- are the molalities of the individual ions; the activity coefficient of the electrolyte, γ , is defined as the geometric mean of the separate activity coefficients, hence

$$\gamma = \sqrt{\gamma_+ \gamma_-} = \sqrt{\frac{a_+}{m_+} \cdot \frac{a_-}{m_-}} = \frac{a_{\pm}}{m_{\pm}} = \frac{\sqrt{k a_2}}{m_{\pm}} \quad (xlii)$$

where m_{\pm} is the mean molality of the two ions. For a solution of a *single* uni-univalent electrolyte m_{\pm} is equal to m .† In general,

* See *Thermodynamics*, 1923, by these authors.

† In a mixture of electrolytes with an ion in common m_+ and m_- represent the *total* molalities of the ions concerned; e.g. for 0.1 molal hydrochloric acid and 0.5 molal barium chloride, m_- (for the chlorine ion) is 1.1, whereas m_+ for H^+ is 0.1, and m_+ for Ba^{++} is 0.5. Hence m_{\pm} for hydrochloric acid is $\sqrt{0.1 \times 1.1}$, and for barium chloride $\sqrt{0.5 \times (1.1)^2}$.

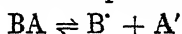
for an electrolyte which dissociates into ν ions, consisting of ν_+ cations and ν_- anions,

$$k = a_+^{\nu_+} a_-^{\nu_-} \quad (\text{xliii})$$

$$a_{\pm} = \sqrt[\nu]{a_+^{\nu_+} a_-^{\nu_-}} = \sqrt[\nu]{k a_2} \quad (\text{xliv})$$

$$\text{and} \quad \gamma = \sqrt[\nu]{\gamma_+^{\nu_+} \gamma_-^{\nu_-}} = \frac{a_{\pm}}{m_{\pm}} = \sqrt[\nu]{\frac{(a_+^{\nu_+} a_-^{\nu_-})}{(\nu_+ m_+)^{\nu_+} (\nu_- m_-)^{\nu_-}}} \quad (\text{xlv})$$

When considering dissociation, or other, equilibria in electrolytes it is more convenient to employ an activity coefficient (f) involving the *actual* concentration of an ion as distinct from its total possible concentration. If the ionization of an electrolyte is considered to be complete, as in the Debye-Hückel theory (Chap. VII), the values of f and γ must be identical; in dilute solutions of strong electrolytes the two quantities cannot differ appreciably in any case. For any particular ion B' the concentration is represented by $[B']$, and the activity by $a_{B'}$, then the activity coefficient $f_{B'}$ is equal to $a_{B'}/[B']$. In applying the law of mass action this nomenclature is frequently used. Thus for the equilibrium



$$\frac{a_{B'} \times a_{A'}}{a_{BA}} = K,$$

where the activity of each species is indicated by a subscript. Then introducing activity coefficients,

$$\frac{f_{B'}[B'] \times f_{A'}[A']}{f_{BA}[BA]} = K$$

$$\text{or} \quad \frac{[B'] [A'] f_{B'} f_{A'}}{[BA] f_{BA}} = K \quad \dots \dots \dots (\text{xlvii})$$

This is an example of the general form of the law of mass action which is always applicable. In most cases, however, the activities are not easily determined and the measured quantity involves the stoichiometric concentrations in square brackets; hence the expression equivalent to

$$\frac{[B'] [A']}{[BA]}$$

is still frequently used. It may be given the symbol k , although, it is only a constant if $f_{B'} \times f_{A'}/f_{BA}$ is constant, thus

$$k \frac{f_{B'} f_{A'}}{f_{BA}} = K \quad \dots \dots \dots (\text{xlvii})$$

K is called the true, or 'thermodynamic', dissociation constant

whereas k is only a constant under very limited conditions; * it is sometimes called the 'classical' dissociation constant. In general the activity coefficient of un-ionized molecules may be taken as unity, hence

$$kf_B \cdot f_A = K$$

The Ionic Strength—In dilute solutions of weak electrolytes f_B and f_A are both very little different from unity, and hence k , the apparent or classical constant, is a true constant. In the presence of strong electrolytes, with or without a common ion, the activity coefficients f_B and f_A are no longer unity; k is then not equal to K , and may not even be constant at different dilutions. Lewis and Randall † have suggested that in dilute solutions the activity coefficient of an ion or electrolyte is the same in all solutions of the same 'ionic strength'. The ionic strength, given the symbol μ , is really a measure of the intensity of the electrical field existing in a solution; it is defined as half the sum of the terms obtained by multiplying the molality (or concentration) of each ion in solution by the square of its valency. Thus in a solution of 0.1 molal hydrochloric acid and 0.5 molal barium chloride the ionic strength is given by:

$$\mu = \frac{1}{2} \{0.1 \text{ (for H')} + 1.1 \text{ (for Cl')} + 0.5 \times 2^2 \text{ (for Ba'')}\} = 1.6.$$

For a weak electrolyte the ionic concentration must be obtained first by multiplying the total concentration by the degree of ionization; strong electrolytes are assumed to be completely ionized.

If the ionic strength of a medium is kept constant, e.g. by the addition of neutral salts, the activity coefficients of the ions remain constant, according to the views of Lewis and Randall. ‡ Hence under these conditions the quantity k will be a constant, although not equal to the true constant K ; the value of k , like the activity coefficients, depends on the actual ionic strength of the solution.

Determination of Activity Coefficients—The most accurate method for the determination of activity coefficients depends on *E.M.F.* measurements, and this will be described later (p. 363); two other methods will be outlined here.

Freezing-Point Method—It has been deduced thermodynamically § for an aqueous solution that

$$d \ln a_2 = \frac{d\theta}{\lambda m} + 0.00057 \frac{\partial d\theta}{\partial m} \quad \dots \quad (\text{xlvi})$$

* When activities are considered the constant will be represented by K , but if concentrations only are employed k will be used.

† *J. Amer. Chem. Soc.*, 1921, 43, 1112.

‡ The Debye-Hückel theory has provided a theoretical basis for this in dilute solutions. The rule is probably applicable, approximately, to both f and γ for strong electrolytes.

§ Lewis and Randall, *Thermodynamics*, 1923, p. 282 et seq.

where a_2 is the activity of the solute, m is the molality of the solution, θ the lowering of freezing-point from that of the pure solvent, and λ is the molal lowering of freezing-point per 1000 gms. of solvent at infinite dilution (1.858° for water); the heat of dilution is ignored in this deduction. For a dilute solution the last term of the equation is very small and may be neglected, hence

$$d \ln a_2 = \frac{d\theta}{\lambda m} \quad (\text{xlix})$$

For an electrolyte which produces ν ions on ionization, it has been shown that $a_{\pm} = \sqrt[\nu]{k a_2}$; hence

$$\ln a_2 = \nu \ln a_{\pm} - \ln k$$

By differentiation $d \ln a_2 = \nu d \ln a_{\pm}$

$$\therefore \nu d \ln a_{\pm} = \frac{d\theta}{\lambda m}$$

$$\text{and } d \ln a_{\pm} = \frac{d\theta}{\nu \lambda m}.$$

A function j may be defined by the expression :

$$j = 1 - \frac{\theta}{\nu \lambda m}$$

so that j becomes zero at infinite dilution, when $\theta = \nu \lambda m$. Differentiating this and simplifying, it is found that

$$\frac{d\theta}{\nu \lambda m} = (1 - j) \frac{dm}{m} - dj$$

$$\therefore d \ln a_{\pm} = (1 - j) \frac{dm}{m} - dj$$

Subtract $d \ln m$ from both sides of this equation, and there results :

$$d \ln \frac{a_{\pm}}{m} = d \ln \gamma = -j \frac{dm}{m} - dj \quad (\text{l})$$

$$\begin{aligned} \therefore \ln \gamma &= - \int_0^m \frac{j}{m} dm - \int_0^m dj \\ &= - \int_0^m \frac{j}{m} dm - j \end{aligned} \quad (\text{li})$$

This equation may be solved if the lowering of the freezing-point of the solution (θ) at various concentrations (molalities) is known; the value of j can then be determined and $-j/m$ plotted against m . The value of the definite integral is the area below this curve between the limits of zero and m . The graphical method is tedious

and a simplification has been suggested. Lewis and Linhart* have found the empirical equation $j = \beta m^\alpha$ to be accurately obeyed in solutions of electrolytes up to 0.01 molal, β and α being constants. The value of these constants may be determined if the freezing-point depressions at various molalities are known. Substituting for j in equation (I) it follows that

$$d \ln \gamma = -\beta m^{\alpha-1} dm - \beta d(m^\alpha),$$

and by integration, $\ln \gamma = -\frac{\beta}{\alpha} m^\alpha - \beta m^\alpha + \text{constant}$.

Since $\ln \gamma$ and m are both zero at infinite dilution ($\gamma = 1$) the integration constant must be equal to zero, hence

$$\log \gamma = -\frac{\beta(\alpha + 1)}{2.303\alpha} m^\alpha = -\beta' m^\alpha \quad \dots \quad (\text{lii})$$

where $\beta' = \frac{\beta(\alpha + 1)}{2.303\alpha}$, which is a constant for a given electrolyte.

The value of β' can be determined from the known values of α and β ; hence the activity coefficient may be calculated for any desired molality up to about 0.01. The accuracy of the results obtained depends on the reliability of the freezing-point measurements in dilute solution.

For more concentrated solutions it is necessary to take into account the quantity $0.0057\theta d\theta/m$ which was originally neglected (equation xlviii); with solutions more concentrated than about 0.5 molal further corrections must be made for the heat of dilution.† If the solution is dilute enough for the heat of dilution to be neglected the activity coefficient is independent of the temperature; in more concentrated solutions, however, the value determined is applicable only at the freezing-point. In order to calculate the activity coefficient at a standard temperature, e.g. 25°, a correction must be applied involving the partial molal heat content of the water in the solution, and also its partial molal heat capacity.‡ The mean activity coefficients given in Table XXV have been obtained from freezing-point measurements.§

It is interesting to note that substances of the same valency type have almost identical activity coefficients, especially in dilute

* *J. Amer. Chem. Soc.*, 1919, 41, 1951; see also Brønsted, *ibid.*, 1922, 44, 938.

† Lewis and Randall, *op. cit.*, p. 348; *J. Amer. Chem. Soc.*, 1921, 43, 1112.

‡ See Lewis and Randall, *op. cit.*, p. 349; *loc. cit.*, p. 1123; see also Young and Vogel (O. G.), *J. Amer. Chem. Soc.*, 1932, 54, 3030.

§ The data have been taken from Lewis and Linhart, *loc. cit.*; Lewis and Randall, *op. cit.*; Randall and Vanselow, *J. Amer. Chem. Soc.*, 1924, 46, 2418; Harned, *ibid.*, 1922, 44, 252; Taylor, *Physical Chemistry*, 1931, p. 769 (Harned).

TABLE XXV
MEAN ACTIVITY COEFFICIENTS FROM FREEZING-POINT DATA

Electrolyte.	Molal Concentration.						
	0.0001	0.0005	0.001	0.005	0.01	0.05	0.1
HCl	0.992	0.981	0.973	0.940	0.916	0.840	0.809
NaCl	0.985	0.972	0.963	0.928	0.906	0.834	0.792
KCl	0.982	0.970	0.961	0.926	0.903	0.821	0.779
KNO ₃	0.994	0.984	0.976	0.943	0.916	0.806	0.732
K ₂ SO ₄	0.935	0.885	0.85	0.75	0.69	0.505	0.421
BaCl ₂	0.94	0.89	0.865	0.77	0.72	0.568	0.501
Pb(NO ₃) ₂	0.965	0.922	0.891	0.773	0.694	0.465	0.369
CuSO ₄	0.85	0.75	0.69	0.50	0.40	0.216	0.158
La(NO ₃) ₃	0.92	0.85	0.81	0.66	0.57	0.391	0.326

solutions. This fact is often used when the activity coefficient of a salt is required for which the necessary measurements have not been made.*

Vapour Pressure Method—For any system obeying the gas laws the activity of each component may be put equal to its concentration; in the case of a mixture of vapours at low pressure, for which the gas laws may be assumed to hold, the partial pressure of each component is proportional to its molecular concentration and so also to its activity. In a solution of two components in equilibrium with their vapours no work can be done by transferring a small quantity of either component from one phase to the other; hence the activity of either component is the same in each phase. It may be seen, therefore, that the activity of each component in a solution is proportional to its partial pressure in the vapour phase. This principle may be used to determine the activity of an electrolyte if it is volatile, and the gas laws are assumed to hold for the vapour. As a general rule such substances are non-volatile, but with aqueous solutions of halogen acids the method may be applied. Consider two solutions of hydrochloric acid of molality m and m' ; the partial pressure of the acid vapour is p and p' respectively, and the activities of the molecules are a_2 and a_2' . Then

$$\frac{p}{p'} = \frac{a_2}{a_2'} = \left(\frac{a_{\pm}}{a_{\pm}'} \right)^2 \quad \text{(lii)}$$

$$\therefore \frac{\gamma}{\gamma'} = \frac{a_{\pm}}{m} \cdot \frac{m'}{a_{\pm}'} = \frac{m'}{m} \sqrt{\frac{p}{p'}} \quad \text{(liv)}$$

* The freezing-point treatment for weak electrolytes is given by Randall and Allen, *J. Amer. Chem. Soc.*, 1930, 52, 1814.

this gives the ratio of the activity coefficients at two concentrations of acid. The value of γ at one definite concentration must be known, and the value at other concentrations may be determined from measurements of the partial pressure of hydrochloric acid above its aqueous solution. For a molar solution, the activity coefficient (γ) has been found by *E.M.F.* measurements to be 0.823; from this value and the partial pressures of various solutions at 25°, Dunn and Rideal* have calculated the mean activity coefficients given in Table XXVI.

TABLE XXVI
ACTIVITY COEFFICIENTS (γ) OF HYDROCHLORIC ACID FROM VAPOUR
PRESSURE DATA

c (gm. mols./litre).	0.4	0.5	0.6	0.75	1.0	2.0	3.0	4.0
γ	0.771	0.757	0.770	0.780	[0.823]	1.02	1.265	1.66

For other methods that may be used to determine activity coefficients various publications of Lewis and Randall, and others should be consulted.†

Activity Coefficients in Mixtures—The general definition for the activity coefficient in a mixture is the same as for a simple electrolyte; the molality m refers, however, to the *total* molality of the particular ion in the mixture. Measurements of activity coefficients in mixtures are generally made by *E.M.F.* methods (p. 366), although a solubility method of limited applicability (p. 128) is available. For dilute solutions the results generally agree with the empirical rule of Lewis and Randall that the activity coefficient is constant at a definite ionic strength; in concentrated solutions, of ionic strength greater than about 0.03, and in solutions containing ions of high valency the rule, although still a useful approximation, fails to hold.‡ In such solutions the ionic strength, which takes into account the number and valency of the ions, but not their own specific properties, is not the only factor affecting the activity of an ion; beyond a certain concentration each ion in the mixture exerts its own special effect. If the ionic strength of a system is kept high and constant, by the addition of a large

* *J. Chem. Soc.*, 1924, 125, 676.

† *Thermodynamics*, 1923, p. 268 *et seq.*; *J. Amer. Chem. Soc.*, 1921, 43, 1112; Randall and White, *ibid.*, 1926, 48, 2514; Randall, *Trans. Faraday Soc.*, 1927, 23, 502; Pearce *et al.*, *J. Physical Chem.*, 1927, 31, 231; *J. Amer. Chem. Soc.*, 1928, 50, 2951; Saxton and Smith (R. P.), *ibid.*, 1932, 54, 2626; Robinson (R. A.) and Sinclair, *ibid.*, 1934, 56, 1830; Åkerlöf and Turck, *ibid.*, p. 1875. See also references on p. 365 *infra*.

‡ Cf. Brønsted, *J. Amer. Chem. Soc.*, 1922, 44, 877; *Trans. Faraday Soc.*, 1927, 23, 416; Brønsted and La Mer, *J. Amer. Chem. Soc.*, 1924, 46, 555; La Mer *et al.*, *ibid.*, 1927, 49, 410; 1928, 50, 2656; see also p. 129 *infra*.

excess of neutral salt, the activity coefficients of ions present in comparatively small amount remain constant; in these circumstances it has been found that the law of mass action is obeyed when ordinary concentration terms are used.* In the absence of an excess of neutral salt the ionic strength of the solution and the activities of the ions vary and the law appears to fail completely.

Activity Coefficients of Individual Ions—The deductions made hitherto have been of the *mean* activity coefficient of the two ions of an electrolyte, and no information has been obtained concerning the activity coefficients of the individual ions. It can, in fact, be shown theoretically that all known methods of measurement yield the mean activity of the electrolyte, and consequently the concept of individual ion activities is mainly of theoretical interest.† According to the simple theory of electrolytic dissociation, propounded by Arrhenius, the 'degree of ionization' as referring to each ion of an electrolyte must naturally be the same; this equality does not necessarily extend to activities. At infinite dilution the activity coefficients of all ions are unity, but at appreciable concentrations the deviations from unity may vary with the nature of the ion.‡

It has been observed that for dilute solutions of uni-univalent chlorides the product of the transport number of the chlorine ion and the equivalent conductance of the solution, at a given concentration, is independent of the nature of the cation.§ This indicates that in a dilute solution the chlorine ion contributes a definite amount towards the conductance of a chloride solution, irrespective of the nature of the other ion. Further, the mean activity of a given chloride in dilute solution depends only on the ionic strength; hence it is reasonable to assume that the activity of the chlorine ion is constant in dilute solutions of different chlorides at the same molal concentrations. The independence of conductance and of activity of a given ion of the nature of the other ions is considered to apply to all ions. It has also been supposed || on the basis of the similarity of weight and mobility of the potassium and chlorine ions, that in a dilute solution of potassium chloride the two ions

* Brønsted and Pedersen, *Z. physikal. Chem.*, 1922, **103**, 307; La Mer and Sandved, *J. Amer. Chem. Soc.*, 1928, **50**, 2656.

† Taylor (P. B.), *J. Physical Chem.*, 1927, **31**, 1478; Guggenheim, *ibid.*, 1929, **33**, 842; *Phil. Mag.*, 1935, **19**, 589.

‡ According to the Debye-Hückel theory (Chapter VII) all ions of the same valency type should have the same activity coefficients, at the same concentrations, provided the solutions are dilute.

§ Lewis, *J. Amer. Chem. Soc.*, 1912, **34**, 1619; MacInnes, *ibid.*, 1919, **41**, 1086; 1921, **43**, 1217.

|| MacInnes, *loc. cit.* It is only by making an arbitrary assumption of this type that any progress at all can be made in connection with individual ion activities. This important limitation must be kept in mind.

have the same activities. For potassium chloride of ionic strength (μ) equal to 0.01, Lewis and Randall take γ as 0.922; hence in accordance with the views expressed $\gamma_{K^+} = \gamma_{Cl^-} = 0.922$ at this ionic strength. For potassium iodate γ , at $\mu = 0.01$, is 0.882, hence

$$\gamma_{KIO_3} = \sqrt{\gamma_{K^+} \times \gamma_{IO_3^-}} = 0.882$$

and since $\gamma_{K^+} = 0.922$, $\gamma_{IO_3^-} = 0.844$

For barium chloride at $\mu = 0.01$, $\gamma = 0.800$ (mean value);

$$\begin{aligned}\gamma_{BaCl_2} &= \sqrt[3]{\gamma_{Ba^{++}} \times \gamma_{Cl^-}^2} \\ \therefore \gamma_{Ba^{++}} &= \frac{(0.800)^3}{(0.922)^2} = 0.603\end{aligned}$$

The activity coefficients of the barium and chlorine ions in a barium chloride solution of ionic strength 0.01 are thus different. For barium iodate at the same ionic strength the mean activity coefficient is given by

$$\begin{aligned}\gamma_{Ba(IO_3)_2} &= \sqrt[3]{\gamma_{Ba^{++}} \times \gamma_{IO_3^-}^2} \\ &= 0.754\end{aligned}$$

The corresponding value determined from solubility measurements of barium iodate in the presence of other electrolytes appears to be 0.746 when $\mu = 0.01$. An additional method is thus made available for determining the activity coefficient of a salt; it requires, however, a knowledge of the coefficients at the same ionic strength of other salts containing ions in common.

Comparison of Activity Coefficient, Conductance Ratio and Osmotic Coefficient—A comparison of accurate data obtained in conductance and freezing-point measurements has shown that the agreement between the so-called degrees of dissociation calculated by these methods is not so good as was originally supposed by Arrhenius (p. 17); in the light of modern theories of electrolytes such an agreement would not be expected. Actually the 'degree of dissociation' calculated from freezing-point measurements (α_0) is related, although by no means equal, to the activity coefficient. Equations (li) and (lii) (p. 117) connect $\log \gamma$ with j , the latter being equal to $1 - i/\nu$, since $\theta/\lambda m$ is equivalent to i , where i is the van 't Hoff factor, and ν the number of ions formed when one molecule of the salt dissociates; it is clear that α_0 , which is equal to $(i - 1)/(\nu + 1)$, cannot be equal to γ . Further, if the conductance ratio, α , is to be attributed to the ratio of the ionic velocities at a given concentration and at infinite dilution, it can have little connection with the activity coefficient. At infinite dilution the values of γ , α and α_0 all become unity; hence it is not surprising that these coefficients are approximately equal in dilute solutions. This is, however, purely fortuitous as divergencies may be observed

even in 0.01*N*-solutions. Activity coefficients greater than unity are very commonly observed in fairly concentrated solutions, but α_0 and α are always less than unity.

The Solubility Product Principle—When a solution is saturated with a given salt MA there is an equilibrium between the solid solute and the dissolved molecules; the activity of the salt is then the same in both conditions. For any saturated solution, therefore, of this salt at a given temperature, irrespective of the presence of other ions or molecules, the activity of the salt molecules remains constant. This activity may be considered as either that of the undissociated molecules or as the mean activity of the ions, viz.

$$a_2 = a \text{ constant}$$

or

$$\sqrt{a_+ a_-} = a \text{ constant.}$$

In either case the same conclusion is reached; since $a_+ a_- = ka_2$, then $a_+ a_-$ is a constant in any case. That is, for a saturated solution of a uni-univalent salt the product of the ionic activities is constant. In the case considered the salt MA ionizes



and the product of ion activities is $a_{M'} \times a_{A'}$; these may be represented in terms of activity coefficients and concentrations, thus

$$a_{M'} = [M']f_{M'} \text{ and } a_{A'} = [A']f_{A'}.$$

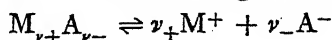
Hence $a_{M'} \times a_{A'} = [M'] [A']f_{M'}f_{A'}$ = a constant. In general for any electrolyte which dissociates into ν_+ cations and ν_- anions, thus: $M_{\nu_+}A_{\nu_-} \rightleftharpoons \nu_+ M^+ + \nu_- A^-$, it follows that in a saturated solution the product $a_+^{\nu_+} a_-^{\nu_-}$ is constant, hence

$$[M^+]^{\nu_+} [A^-]^{\nu_-} \cdot (f_{M^+})^{\nu_+} (f_{A^-})^{\nu_-} = a \text{ constant. } (K_s) \quad (\text{lv})$$

In very dilute solution, for example when dealing with a sparingly soluble salt in the absence of appreciable amounts of other electrolytes, the ionic activity coefficients f_{M^+} and f_{A^-} may be regarded as constant—almost unity—and under such conditions

$$[M^+]^{\nu_+} [A^-]^{\nu_-} = a \text{ constant. } (k_s) \quad (\text{lv})$$

This result expresses the solubility product principle deduced by Nernst,* the constant being called the **solubility product** of the salt. In the original deduction Nernst applied the law of mass action to the ionization of the salt, using concentration terms; thus



$$\therefore \frac{[M^+]^{\nu_+} [A^-]^{\nu_-}}{[M_{\nu_+}A_{\nu_-}]} = \text{constant.}$$

* *Z. physikal. Chem.*, 1889, 4, 372; for alternative deductions see Washburn, *J. Amer. Chem. Soc.*, 1910, 32, 488; Butler, *Chem. and Ind.*, 1924, 43, 634; *J. Physical Chem.*, 1924, 28, 438.

The concentration of undissociated salt $[M_{\nu+}A_{\nu-}]$ in a saturated solution was then assumed to be constant; hence

$$[M^{+}]^{\nu+}[A^{-}]^{\nu-} = \text{a constant. (Solubility product, } k_s) \quad (\text{lvii})$$

In the light of present-day theories it may be concluded that the solubility product, as defined in this way, can only be constant when the activity coefficients are constant, i.e. when the solution is very dilute, or the ionic strength is kept constant. In spite of this limitation the solubility product principle in its approximate form has proved of very great value in analytical chemistry.* It indicates, for example, that the presence of a salt with a common ion will reduce the solubility of a sparingly soluble salt; thus silver chloride is less soluble in potassium chloride, or in silver nitrate solutions, than it is in water. The presence of excess of the common ion means that the concentration of the other ion must be reduced in order that the solubility product may be kept constant; this can only occur if some of the saturating salt is thrown out of solution. The decrease of solubility may be calculated as follows:

Let S_0 equal the solubility of silver chloride in water, then if it may be assumed to be completely dissociated, $[Ag^+] = [Cl^-] = S_0$; hence the solubility product k_s is equal to S_0^2 . Suppose x gm. equiv. of a chloride (e.g. KCl), which is supposed to be completely dissociated, is added to a litre of solution; this adds x gm. ions of chlorine to the solution, and the solubility of the silver chloride is decreased to S . The value of $[Ag^+]$ is now S , but the value of $[Cl^-]$ is $S + x$; hence

$$S(S + x) = k_s = S_0^2$$

$$S = \frac{x}{2} + \frac{1}{4} - S_0^2 \quad (\text{lviii})$$

Using equations of this type, or modified for incomplete dissociation of the various salts, the solubilities of sparingly soluble salts in the presence of electrolytes with a common ion have been calculated † and have been found in many cases to be in agreement with experimental results. Some instances were found, however, in which the simple solubility product principle was not satisfactory; e.g. the solubility of lanthanum iodate is decreased by the addition of sodium iodate, but the addition of lanthanum nitrate causes the solubility first to decrease and then to increase.‡ Further,

* See, for example, Bassett, *The Theory of Quantitative Analysis*; Smith (T. B.), *Analytical Processes*.

† Nernst, *Z. physikal. Chem.*, 1889, 4, 372; Noyes, *ibid.*, 1890, 6, 241; Creighton and Ward, *J. Amer. Chem. Soc.*, 1915, 37, 2333.

‡ Harkins and Pearce, *ibid.*, 1916, 38, 2679; see also, Åkerlöf and Thomas, *ibid.*, 1934, 56, 593, for solubility of silver sulphate in sulphate solutions.

although the principle may be satisfactory qualitatively, it was found that the product of the ionic concentrations is not a constant as the theory requires.* The fundamental assumptions on which the principle was deduced were also shown to be erroneous; in the first place the simple law of mass action does not apply to strong electrolytes,† and in the second place it was found that the solubility of a salt could be reduced *below* the so-called constant concentration of undissociated salt!‡

It had been known for some time that in the presence of a neutral salt without a common ion the solubility of a sparingly soluble salt was often increased; to account for this the following theory was proposed. If AB is the sparingly soluble salt and CD the neutral salt, the formation of undissociated AD and CB will result in the removal of A^+ and B^- ions from solution; hence more AB will dissolve to maintain the constancy of the solubility product. Several cases were found, however, in which the solubility decreased, after increasing, on the continued addition of electrolyte without a common ion.§

Most of the phenomena in connection with the solubility of sparingly soluble salts can be quite satisfactorily explained if the activity coefficients of the ions are taken into consideration. The addition of a common ion invariably increases the total activity of that ion, and so the activity of the other ion must decrease in order to maintain the activity solubility product constant; the solubility then diminishes. It will be seen, however, that this decrease may not necessarily go on continuously. The product $[M'] [A'] f_M f_A$ must remain constant, when $[M']$, say, is augmented by the addition of another salt; but the increase of ionic strength will cause both f_M and f_A to decrease, and a point may, therefore, be reached when the quantity $[A']$ will have to increase, in spite of the increase of $[M']$. The solubility of MA will then commence to rise; such a condition is not often reached, as the activity coefficients fall to a minimum and then increase with increasing ionic strength.|| In any case if the actual solubility does not rise, the product of $[M']$ and $[A']$ must increase as the activity coefficients of the ions decrease with increasing ionic strength; this accounts for one of the chief weaknesses of the simple solubility product principle.

* Hill, *ibid.*, 1910, 32, 1186; Noyes *et al.*, *ibid.*, 1911, 33, 1643, 1650, 1671.

† Cf. Stieglitz, *ibid.*, 1908, 30, 946.

‡ Arrhenius, *Z. physikal. Chem.*, 1899, 31, 197; Noyes, *ibid.*, 1905, 52, 636; Kendall and Andrews, *J. Amer. Chem. Soc.*, 1921, 43, 1545.

§ Cameron, *J. Physical Chem.*, 1901, 5, 556; Hill and Simmons, *J. Amer. Chem. Soc.*, 1909, 31, 821.

|| See, however, Harkins and Pearce, *loc. cit.*; Kendall and Andrews, *loc. cit.*

The lowering of the total solubility of the salt below a certain value is not contrary to the idea of activity product constancy; theoretically there is no lower limit to the solubility. The theory postulates that the *activity* of the undissociated salt is constant in a saturated solution, but this activity has no simple connection with the concentration, especially if the ionic strength of the solution is altered. The effect of a neutral salt, without a common ion, is to increase the ionic strength, and hence to decrease the activity coefficients of both ions of the sparingly soluble salt; the solubility of the latter must increase in order that $[M^+][A^-]f_{M^+}f_{A^-}$ may be kept constant. As a general rule the higher the valency of the ions of the neutral salt the greater the lowering of the activity coefficient, and so the more will the solubility increase. At high ionic strengths the activity coefficients commence to increase, hence the solubility of the saturating salt will decrease.

Solubility Product and Solubility—If the salt, $M_{\nu+}A_{\nu-}$ is completely ionized and its solubility is S gm. mols. per litre, then $[M^+]$ and $[A^-]$ are equal to ν_+S and ν_-S gm. ions respectively. Hence

$$K_s = [M^+]^{\nu+}[A^-]^{\nu-} \cdot (f_{M^+})^{\nu+}(f_{A^-})^{\nu-} \\ = (\nu_+S)^{\nu+}(\nu_-S)^{\nu-} \cdot (f_{M^+})^{\nu+}(f_{A^-})^{\nu-} \quad \dots \quad (\text{lix})$$

In the simple case when activity coefficients are assumed to be equal to unity—this is approximately true in a solution of a sparingly soluble compound containing no added salts—the solubility and solubility product are related by the expression

$$k_s = (\nu_+)^{\nu+}(\nu_-)^{\nu-} \cdot S^{\nu}, \quad \dots \quad (\text{lx})$$

where ν is equal to $\nu_+ + \nu_-$. For a uni-univalent electrolyte, $\sqrt{k_s} = S$; this formula is frequently used to obtain solubilities from solubility products, since the latter can be determined from *E.M.F.* measurements (p. 368).

With two solutions I and II which may contain neutral salts, but not with an ion in common with the sparingly soluble compound,

$$K_s = (\nu_+)^{\nu+}(\nu_-)^{\nu-} \cdot S_I^{\nu} (f_{M^+})_I^{\nu+} (f_{A^-})_I^{\nu-}$$

holds for one solution, and

$$K_s = (\nu_+)^{\nu+}(\nu_-)^{\nu-} \cdot S_{II}^{\nu} (f_{M^+})_{II}^{\nu+} (f_{A^-})_{II}^{\nu-}$$

for the other. Hence

$$\left(\frac{S_I}{S_{II}} \right)^{\nu} = \frac{(f_{M^+})_{II}^{\nu+} (f_{A^-})_{II}^{\nu-}}{(f_{M^+})_I^{\nu+} (f_{A^-})_I^{\nu-}} = \frac{f_{\pm II}^{\nu}}{f_{\pm I}^{\nu}}$$

and

$$\frac{S_I}{S_{II}} = \frac{f_{\pm II}}{f_{\pm I}} \quad (\text{lx})$$

where $f_{\pm I}$ and $f_{\pm II}$ are the mean activity coefficients of the salt MA in the two solutions. In the absence of a common ion, therefore, the solubility of the substance in any solution is inversely proportional to its activity coefficient or to the mean activity coefficient of its ions in that solution.

The Principle of Specific Interaction of Ions—An important contribution to the theory of the influence of neutral salts on solubility was made by Brønsted; * the fundamental assumption of the principle is that, since ions of the same sign repel one another and so will be relatively far apart, deviations from ideal behaviour are due to ions of opposite sign. If a sparingly soluble salt MA is dissolved in two solutions containing the salts X_1Y and X_2Y , respectively, with an anion (Y) in common at *equivalent concentrations*, then the ratio of the activity coefficient of M^+ ions in the two solutions is a function of the nature of the cations X_1 and X_2 , only; thus

$$\frac{f_{M^+}(X_1Y)}{f_{M^+}(X_2Y)} = F(X_1, X_2).$$

The ratio of the activity coefficient of the anion A^- is a function of its own nature and of the oppositely charged ions X_1 and X_2 ; thus

$$\frac{f_{A^-}(X_1Y)}{f_{A^-}(X_2Y)} = F(X_1, X_2, A).$$

Since the mean activity coefficient (f) of MA, assumed to be a uni-univalent salt, is equal to $(f_{M^+} \cdot f_{A^-})^{\frac{1}{2}}$, the ratio in the two solutions is a function of X_1 , X_2 and A , that is

$$\frac{f_{MA}(X_1Y)}{f_{MA}(X_2Y)} = F_1(X_1, X_2, A).$$

The ratio of the solubility of MA in the two solutions, containing X_1Y and X_2Y respectively, is inversely proportional to the activity coefficients; hence

$$\frac{S_{MA}(X_1Y)}{S_{MA}(X_2Y)} = F_2(X_1, X_2, A).$$

Consider the definite case in which MA is silver chloride, and X_1Y and X_2Y are sodium and potassium nitrate respectively, then

$$\frac{S_{AgCl}(NaNO_3)}{S_{AgCl}(KNO_3)} = F_2(Na, K, Cl).$$

* *Ibid.*, 1922, 44, 877; 1923, 45, 2898; *Trans. Faraday Soc.*, 1927, 23, 420; see also Güntelberg, *Z. physikal. Chem.*, 1926, 123, 199; La Mer *et al.*, *J. Amer. Chem. Soc.*, 1929, 51, 2622, 2632; 1931, 53, 103; Scatchard and Prentiss, *ibid.*, 1934, 56, 2320; Harned, *ibid.*, 1935, 57, 1865; Guggenheim, *Phil. Mag.*, 1935, 19, 589.

Similarly if MA were thallous chloride,

$$\frac{S_{\text{TlCl}(\text{NaNO}_3)}}{S_{\text{TlCl}(\text{KNO}_3)}} = F_2(\text{Na}, \text{K}, \text{Cl}),$$

and even if X_1Y and X_2Y were sodium and potassium chlorate or sulphate, the ratio would be the same since *the common anion does not influence the activity coefficient ratio*. Hence

$$\frac{S_{\text{AgCl}(\text{NaNO}_3)}}{S_{\text{AgCl}(\text{KNO}_3)}} = \frac{S_{\text{TlCl}(\text{NaClO}_3)}}{S_{\text{TlCl}(\text{KClO}_3)}} = \frac{S_{\text{TlCl}(\text{NaNO}_3)}}{S_{\text{TlCl}(\text{KNO}_3)}} = \frac{S_{\text{AgCl}(\text{Na}_2\text{SO}_4)}}{S_{\text{AgCl}(\text{K}_2\text{SO}_4)}}. \quad (\text{Ixii})$$

When the two salt solutions have a cation in common, e.g. XY_1 and XY_2 , it may be shown in an exactly similar manner, that

$$\frac{S_{\text{MA}(\text{XY}_1)}}{S_{\text{MA}(\text{XY}_2)}} = F_2(X_1, X_2, M).$$

Hence

$$\frac{S_{\text{AgCl}(\text{KNO}_3)}}{S_{\text{AgCl}(\text{KClO}_3)}} = \frac{S_{\text{AgCl}(\text{NaNO}_3)}}{S_{\text{AgCl}(\text{NaClO}_3)}} = \frac{S_{\text{AgBr}(\text{KNO}_3)}}{S_{\text{AgBr}(\text{KClO}_3)}}. \quad (\text{Ixiii})$$

These equations are a valuable guide to the influence of electrolytes on solubility; they have been verified for saturating salts and added salts of various types.* It should be emphasized again that the added salts are assumed to be present at equivalent concentrations.

Determination of Activity Coefficients by Solubility Method—For a uni-univalent electrolyte the activity solubility product may be written

$$(c_+\gamma_+)(c_-\gamma_-) = K_s$$

where c_+ and c_- are the ionic concentrations; this equation holds irrespective of the presence of common or other ions. The mean ionic concentration c_{\pm} is equal to $(c_+c_-)^{\frac{1}{2}}$, and the mean activity coefficient γ_{\pm} is equal to $(\gamma_+\gamma_-)^{\frac{1}{2}}$; hence

$$c_{\pm}\gamma_{\pm} = \sqrt{K_s}$$

and

$$\gamma_{\pm} = \sqrt{K_s}/c_{\pm} \quad \dots \quad (\text{Ixiv})$$

If the activity coefficient and the solubility (S) of a sparingly soluble salt, in the absence of any other electrolyte, are known, K_s may be calculated since under these conditions c_{\pm} is equal to S . It is then possible to determine the activity coefficient of the salt in the presence of other salts, with or without a common ion. If K_s is not known it may be determined by plotting the value of c_{\pm} , in the presence of various salts, against the ionic strength, or some other function of the total ionic concentration of the solution; the curve is extrapolated to zero concentration when γ_{\pm} is equal to unity, and c_{\pm} is then equal to $\sqrt{K_s}$ (equation Ixiv).

* See references at beginning of section.

The published data on the solubility of thallous chloride have been used by Lewis and Randall * to calculate the activity coefficient of that salt in the presence of various electrolytes. By plotting c_{\pm} against the ionic strength and extrapolating, the value of $\sqrt{K_s}$ was found to be 0.01428 at 25°; hence it follows that in all solutions $\gamma_{\pm} = 0.01428/c_{\pm}$. The solubility of thallous chloride in a solution of thallous sulphate containing 0.1 gm. equiv. per litre is 0.00468 gm. equiv. at 25°; c_{+} may then be taken as $0.1 + 0.00468 = 0.10468$, whereas c_{-} is 0.00468, and so c_{\pm} is $(0.10468 \times 0.00468)^{\frac{1}{2}} = 0.02213$. The activity coefficient in this solution is then $0.01428/0.02213$, that is 0.643. In Table XXVII are given some of the values of the activity coefficient of thallous chloride at 25° in the presence of various electrolytes, calculated in the manner indicated. It is important to remember that this method only gives the activity coefficient of a salt in its *saturated solution*; hence it is of limited application, although the results are of interest.

TABLE XXVII

ACTIVITY COEFFICIENTS OF THALLOUS CHLORIDE AT 25° (IN THE PRESENCE OF OTHER ELECTROLYTES)

Total Concentration		Nature of Electrolyte				
		KNO ₃	KCl	HCl	TlNO ₃	Tl ₂ SO ₄
† 0.01N	.	0.909	0.909	0.909	0.909	0.909
0.02	.	0.872	0.871	0.871	0.869	0.885
0.05	.	0.809	0.797	0.798	0.784	0.726
0.1	.	0.742	0.715	0.718	0.686	0.643
0.2	.	0.676	0.613	0.630	0.546	—

If the values for the activity coefficient of thallous chloride are plotted against the ionic strength of the solution, it is found that the curves for the various electrolytes are of a uniform type, and approach one another in dilute solution. This coincidence of the curves in dilute solution ($c = 0.01$, and below) confirms the empirical rule that the activity coefficient is a function of the ionic strength only.

For hydrochloric acid and potassium chloride solutions the rule applies up to 0.1N, and it has been claimed by Blayden and Davies ‡ that if allowance be made for the incomplete dissociation of the other added salts, the dependence of the activity coefficient on the ionic strength only, extends to the same concentration.

Complex Ions §—In many instances the addition of a salt with a common ion causes a marked increase in solubility of a

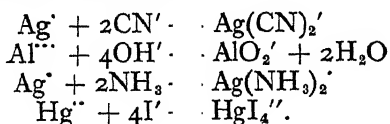
* *J. Amer. Chem. Soc.*, 1921, 43, 1112.

† Activity coefficients obtained by extrapolation.

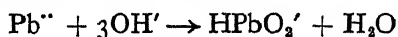
‡ *J. Chem. Soc.*, 1930, 949; see also Davies, *ibid.*, pp. 2410, 2421.

§ See Jacques, *Complex Ions in Aqueous Solutions*, 1914.

sparingly soluble substance; for example silver cyanide is readily soluble in alkali cyanide solutions; aluminium hydroxide is soluble in sodium hydroxide; silver oxide dissolves in ammonia, and mercuric iodide is soluble in potassium iodide. In each case the increase of solubility is due to the removal of the simple ions in the form of complex ions; thus

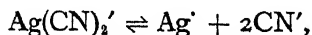


More of the insoluble compound then dissolves and ionizes in order to maintain the solubility product. Silver cyanide will continue to dissolve in potassium cyanide until the free cyanide ion concentration has been reduced to such an extent that it has no further tendency to remove silver ions; the solubility product of silver cyanide may then be reached. For similar reasons nearly all sparingly soluble silver salts will dissolve in potassium cyanide; if, however, the solubility product is very small, e.g. with silver sulphide, an inappreciable amount of the salt will dissolve before the ionic concentrations reach the value required by the solubility product principle. The formation of the HPbO_2' anion from plumbous and hydroxyl ions, thus

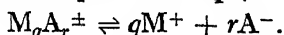


is the cause of the solubility of all lead salts, except the sulphide, in sodium hydroxide solution. Mercuric oxide is soluble in potassium iodide, and many silver salts are soluble in ammonia, because the simple ions are in each case removed as complex ions; these phenomena are of great importance in analytical chemistry.

As a rule the major portion of the metal present in solution can be shown by transference observations (p. 40) to be in the complex ion, but the solution always contains a certain proportion of the simple ions. Even in the very stable argentocyanide solution the addition of sulphuretted hydrogen produces a precipitate of silver sulphide, suggesting that silver ions are present. It is probable that there is always an equilibrium between simple and complex ions, thus:



or, in general, for the complex ion M_qA_r^\pm



If the law of mass action may be applied to this equilibrium, then

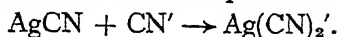
$$K = \frac{a_{\text{M}^+}^q \times a_{\text{A}^-}^r}{a_{\text{M}_q\text{A}_r}}, \quad (\text{lxv})$$

or using concentrations, as is generally done, instead of activities, the approximate equation

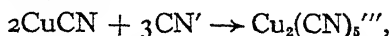
$$k = \frac{[M^+]^q[A^-]^r}{[M_qA_r^\pm]} \quad \dots \quad (\text{lxvi})$$

is obtained. The quantity k is called the 'instability constant' of the complex ion; * this constant is of great value in determining the formula of a complex ion. The greater the instability constant the more the tendency of the complex ion to dissociate into its constituent ions.

Formula of a Complex Ion—Chemical Method—This can only be used if the complex ion is stable, otherwise the results may be misleading. For example, 1 gm. equiv. of alkali cyanide will just dissolve 1 gm. equiv. of silver cyanide; hence it may be assumed that the formula of the complex ion is $\text{Ag}(\text{CN})_2'$, thus



The method must, however, be used with caution: 2 gm. equiv. of cuprous cyanide require 3 gm. equiv. of potassium cyanide for complete dissolution, thus

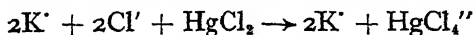


whereas one gm. equiv. of cobaltous cyanide also requires 3 gm. equiv. of alkali cyanide



There is very little doubt, as shown by *E.M.F.* measurements, that the cobaltocyanide complex is $\text{Co}(\text{CN})_5'''$, but copper forms a mixture of two complexes $\text{Cu}(\text{CN})_2'$ and $\text{Cu}(\text{CN})_3''$; † the formulæ obtained from chemical considerations should, therefore, always be verified.

Osmotic Method—This is limited to stable complexes formed from *soluble* substances, e.g. silver nitrate and ammonia, mercuric chloride and potassium chloride. Consider the latter example: if the potassium chloride is dissolved in water it will ionize and produce a definite osmotic effect, e.g. lowering of the freezing-point. If mercuric chloride is added, however, the reaction



occurs, and there is actually a *decrease* in the number of ions present and in the osmotic effect. Further addition of mercuric salt causes a further diminution until the whole of the potassium chloride has formed the complex salt; subsequent portions of

* See Bodländer, *Ber.*, 1903, 36, 3933; actually Bodländer defined the *reciprocal* of this quantity as the 'stability constant'.

† Glasstone, *J. Chem. Soc.*, 1929, 706; Glasstone and Speakman, *Analyst*, 1930, 55, 93.

mercuric chloride will dissolve and exert an independent osmotic influence and so the effect will increase. In this particular instance 1 gm. mol. of mercuric chloride is required for every 2 gm. mols. of potassium chloride before the osmotic effect begins to increase; hence the complex ion formed is HgCl_4^{2-} . Had the formula of the complex been HgCl_3^- the continued addition of mercuric chloride would have had no influence on the osmotic effect until complex formation was complete.* A conductance method based on the principles described here can sometimes be used to determine the formula of a complex ion.

Solubility Method—This may be illustrated by reference to the silver-ammonia complex ion; suppose m gm. ions of silver combine with n gm. mols of ammonia to form the complex $\text{Ag}_m(\text{NH}_3)_n^+$. The instability constant is given by

$$k_i = \frac{[\text{Ag}^+]^m [\text{NH}_3]^n}{[\text{Ag}_m(\text{NH}_3)_n^+]} \quad (\text{lxvii})$$

If a solution of ammonia is saturated with silver chloride then by the solubility product principle, in its approximate form, $[\text{Ag}^+][\text{Cl}^-]$ is equal to k_s ; hence $[\text{Ag}^+] = k_s/[\text{Cl}^-]$, and

$$k_i = \frac{k_s^m \times [\text{NH}_3]^n}{[\text{Cl}^-]^m [\text{Ag}_m(\text{NH}_3)_n^+]} \quad (\text{lxviii})$$

The concentration (c) of the silver salt in the solution may be regarded as consisting entirely of the complex ion, since the normal solubility of the chloride is very small; the concentration of chlorine ions may be taken to be the same, and so

$$k_i = \frac{k_s^m \times [\text{NH}_3]^n}{c^{m+1}} \quad (\text{lix})^\dagger$$

or
$$\frac{[\text{NH}_3]^n}{c^{m+1}} = \text{a constant} \quad (\text{lxix})$$

With this equation the value of $n/(m+1)$ may be determined from a number of solubility measurements. In order to evaluate m it is necessary to determine the solubility of silver chloride in ammonia in the presence of an excess of chlorine ions; then equation (lxviii) takes the form

$$\frac{[\text{NH}_3]^n}{[\text{Cl}^-]^m c} = \text{a constant} \quad (\text{lxxi})$$

* For applications see Reychler, *Bull. Soc. Chim.*, 1895, 13, 386; Euler, *Ber.*, 1903, 36, 1854, 3400; Sherrill, *Z. physikal. Chem.*, 1903, 43, 705; Urbain and Cornec, *Compt. rend.*, 1922, 175, 1406; Bourion and Rouyer, *Ann. Chim.*, 1928, 10, 182 (review).

† This equation may be made slightly more accurate by introducing an approximate value for the activity coefficient of the salt $\text{Ag}_m(\text{NH}_3)_n\text{Cl}$; the omission is not, however, serious since the treatment is approximate.

If in a series of experiments the concentration of ammonia is kept constant then $[\text{Cl}^-]^m c$ is constant, and m may be determined. Alternatively solubility measurements of silver chloride in ammonia in the presence of excess of silver nitrate could be used; the value of $[\text{Ag}^+]$ is equal to the concentration of the latter, and the solubility of the chloride gives the concentration of the complex ion.*

Complex Ions in Solutions of Single Electrolytes—Many apparently simple salts, e.g. cadmium iodide, produce complex ions in solution (p. 40), and it is very probable that such complex formation is quite common, especially in concentrated solutions containing high valency ions.† These complexes are, however, comparatively unstable and the solution contains a large proportion of the simple ions. The so-called 'double salts', e.g. alum, may be regarded as extreme cases in which the complex ion is very unstable; only in concentrated solutions of such substances can any quantity of complex ions be detected by transference measurements.

* For applications see Bodländer and Fittig, *Z. physikal. Chem.*, 1902, 39, 597; Euler, *Ber.*, 1903, 36, 3400; Sherrill, *loc. cit.*; for *E.M.F.* method see p. 400 *infra*; for other methods of investigating complex ions, see Yajnik and Uberoy, *J. Amer. Chem. Soc.*, 1924, 46, 802; Carter and Megson, *J. Chem. Soc.*, 1927, 2023; Job, *Ann. Chim.*, 1928, 9, 113.

† Donnan and Bassett, *J. Chem. Soc.*, 1902, 81, 939; Abegg and Labendzinski, *Z. Elektrochem.*, 1904, 10, 77; Denham, *Z. physikal. Chem.*, 1909, 65, 641; Howell, *J. Chem. Soc.*, 1927, 158; see also references on p. 175 *infra*, and p. 40 *supra*.

CHAPTER VII

THE MODERN DISSOCIATION THEORY

THEORY of Complete Ionization—Although the view that strong electrolytes are almost completely dissociated at all dilutions had been put forward tentatively by several writers,* it was not until recent years that developments in the field of X-ray crystallography and in the electronic theory of valency made this view appear plausible. From the X-ray examination of crystals of alkali halides † it was concluded, and subsequently confirmed by a study of other salts, that the molecule was not the unit of structure in the crystal lattice. Actually the salt crystal is made up of two interlacing lattices, one containing only the positive radical (i.e. metal) and the other only the negative (i.e. acid) radical of the salt. A sodium chloride crystal consists of a face-centred sodium lattice and a face-centred chlorine lattice, but there is no evidence of a sodium chloride molecular lattice; each sodium is surrounded by six chlorines, and each chlorine by six sodiums. Various investigators have confirmed this conclusion and have found similar structures for a large number of salts.

Crystal Structure, Electrovalency and Ionization—This view of the structure of a salt crystal is in harmony with the modern ideas based on the electronic theory of valency; ‡ the union between an atom of sodium and one of chlorine is considered to be accompanied by the transfer of an electron from the former to the latter. In this way two ions with very stable electronic arrangements result, and are held together merely by electrostatic attraction of the oppositely charged ions. This is quite distinct from the co-valent linkage between two atoms when electrons are actually *shared*, and not transferred completely from one atom to the other. According to the theory, as developed by Langmuir,

* Noyes, *Science*, 1904, 20, 582, for abstracts see *Technology Quart.*, 1904, 17, 306; *Z. physikal. Chem.*, 1904, 52, 635; Lewis, *ibid.*, 1909, 70, 212; Sutherland, *Phil. Mag.*, 1906, 12, 1; Bjerrum, *Proc. 7th Int. Congress of App. Chem.*, 1909; Milner, *Phil. Mag.*, 1912, 23, 551; 1913, 25, 742; see van Laar, *Z. anorg. Chem.*, 1924, 139, 108 for historical survey.

† W. H. Bragg and W. L. Bragg, *Proc. Roy. Soc.*, 1913, 89 A, 248.

‡ See Langmuir, *J. Amer. Chem. Soc.*, 1919, 41, 868.

solvent. Hence if the virial term could be evaluated it should be possible to calculate the actual molar depression of the freezing point produced by an electrolyte.

The method of calculating the virial was as follows : by assuming that the Boltzmann principle of the distribution of molecules in a region of varying field of force applied to ions existing in a space of varying electrical potential due to their own attractions and repulsions, it was found that the ions were not distributed uniformly in space. If this is the case it can be shown that the virial is not zero, and hence the behaviour of the electrolyte cannot be ideal. Milner then proceeded to sum the products of the mutual attraction of a pair of ions by their distance apart, for each pair of ions existing in a particular configuration ; the sum was then multiplied by the probability of the occurrence of this configuration, and the results added for every possible configuration of the ions in the solution. Numerical values for the virial term were calculated for different concentrations of a uni-univalent electrolyte, and the corresponding molar freezing-point depressions were evaluated. The results obtained were in excellent agreement with the experimental observations for sodium and potassium chlorides, and in general agreement with those for ammonium chlorides and various nitrates. Later, Milner * discussed the application of the theory of complete ionization to the conductance of electrolytes, but was unable to deduce an equation connecting the conductivity with the dilution. Owing to the very complicated mathematical and arithmetical treatment involved in Milner's deductions his extremely important work did not receive the attention which it merited.

The Theory of Ghosh—The complete ionization theory was revived in a modified form and a simple mathematical treatment was developed by Ghosh ; † the theory involved the following postulates : (a) only ions can exist in solution, and the attraction between oppositely charged ions is governed by the inverse square law ; (b) the arrangement of the ions is analogous to that in a cubic crystal ; (c) each pair of oppositely charged ions forms an electrically saturated neutral doublet ; (d) an ion is free to move only when its kinetic energy is greater than half the work required to separate it from its partner ; and (e) the distribution of velocities is in accordance with Maxwell's law. On the basis of these assumptions Ghosh deduced for uni-univalent electrolytes the formula

$$\frac{N\varepsilon^2 \cdot \sqrt[3]{2N}}{D\sqrt[3]{v}} = 2RT \ln \frac{\Lambda_0}{\Lambda} \quad (\text{iii})$$

where N is the Avogadro number, ε the electronic charge, D the

* *Phil. Mag.*, 1918, 35, 214, 352.

† *J. Chem. Soc.*, 1918, 113, 449, 627, 707, 790.

dielectric constant of the solvent, and v the dilution in cubic centimetres. This equation was claimed to be in excellent agreement with the measurements of Kohlrausch. The theory was criticized by various authors; * in the first place it was doubted if Maxwell's distribution law was applicable to charged particles, and even if it were, the calculation of Ghosh based on this law was erroneous. Further, it was shown that apart from postulate (b) being improbable it was not compatible with postulate (c). After making various necessary corrections the agreement between observed and calculated values, based on the Ghosh formula, were not as good as had been claimed; the theory of Ghosh, although it met with a great deal of approval when first proposed, soon fell into disrepute.

The Debye-Hückel Theory—In 1923 Debye and Hückel † developed the inter-ionic attraction theory of Milner in a more direct form. The fundamental idea underlying the treatment is that owing to electrical attractions between positive and negative ions there are, on the average, in the neighbourhood of any ion more ions of unlike than of like sign; every ion may, therefore, be regarded as being surrounded by an 'ionic atmosphere' of opposite charge. Consequently when a solution is diluted the separation of the ions involves doing internal work against electrostatic attraction in addition to the purely osmotic work of dilution. The theory, therefore, assumes complete ionization and attributes deviations from ideal behaviour to the inter-ionic attractions.

Consider a small volume element dv at a distance r from a positive ion, considered as a point charge, and let ψ represent the average electrical potential in this element. The work required to bring an ion from infinity up to the given volume element is $(z_+e\psi)dv$ if the ion is positively charged, and $-(z_-e\psi)dv$ for a negative ion, where z_+ and z_- are the *numerical* values of the valency of the positive and negative ion, respectively, and e is the electronic charge. By applying the Boltzmann distribution law, as did Milner, it fol-

* Partington, *Trans. Faraday Soc.*, 1919, 15, 110, 162; Chapman and George, *Phil. Mag.*, 1921, 41, 799; Kallmann, *Z. physikal. Chem.*, 1921, 98, 433; Kraus, *J. Amer. Chem. Soc.*, 1921, 43, 2514; Kendall, *ibid.*, 1922, 44, 717; Arrhenius, *Z. physikal. Chem.*, 1922, 100, 9.

† *Physikal. Z.*, 1923, 24, 185, 334; *Rec. trav. chim.*, 1923, 42, 597; *Physikal. Z.*, 1924, 25, 97; Hückel, *Erg. der Exakt. Naturwiss.*, 1925, 3, 199. For alternative lines of treatment, see Noyes, *J. Amer. Chem. Soc.*, 1924, 46, 1080; 1926, 48, 621; Güntelberg, *Z. physikal. Chem.*, 1926, 123, 241; Wheeler, *Physikal. Z.*, 1931, 32, 674; van Rysselberghe, *J. Chem. Physics*, 1933, 1, 205; 1934, 2, 350; Levine, *Proc. Roy. Soc.*, 1935, 152 A, 529. The Debye-Hückel theory has been applied to solutions of ampholytes (Kirkwood, *J. Chem. Physics*, 1934, 2, 351, 713) and to colloidal electrolytes (Hartley, G. S., *Trans. Faraday Soc.*, 1935, 31, 31). For general reviews, see Schingnitz, *Z. Elektrochem.*, 1930, 36, 861; Williams (J. W.) *Chem. Reviews*, 1931, 8, 303; see also references on p. 157.

lows that the number of positive (n_+) and negative (n_-) ions in the volume element is given by *

$$n_+ = ne^{-(z_+e\psi/kT)} dv \quad \dots \quad (iv)$$

$$n_- = ne^{-(-z_-e\psi/kT)} dv \quad \dots \quad (v)$$

where n is the *total* number of ions per c.c., e is the base of natural logarithms, k is the Boltzmann constant, that is the gas constant per single molecule, and T is the absolute temperature. The density of electricity (ρ) is equal to the excess of positive over negative electricity per unit volume, and so in the element under consideration

$$\rho = \frac{n_+e dv - n_-e dv}{dv} \quad \dots \quad (vi)$$

For a uni-univalent electrolyte, both z_+ and z_- are equal to unity, and by introducing the values of n_+ and n_- from equations (iv) and (v) into equation (vi), it follows that

$$\rho = ne(e^{-e\psi/kT} - e^{e\psi/kT}) \quad \dots \quad (vii)$$

Expanding the exponential series, and writing x for $e\psi/kT$, equation (vii) takes the form

$$\rho = -\frac{\varepsilon^2\psi}{kT} 2n \left(1 + \frac{x^2}{3!} + \frac{x^4}{5!} + \dots \right) \quad \dots \quad (viii)$$

If now the assumption, for which there may be little justification (see p. 153), be made that x , that is $e\psi/kT$, is much smaller than unity, equation (viii) may be simplified to

$$\rho = -\frac{\varepsilon^2\psi}{kT} 2n \quad \dots \quad (ix)$$

In the general case, when z_+ and z_- are not necessarily unity, the density of electricity as given by equation (vii) becomes

$$\rho = e \sum n_i z_i e^{-z_i e\psi/kT} \quad \dots \quad (x)$$

where n_i and z_i represent the number per c.c. and valency, respectively, of the ions of the i th kind. Expanding the series and neglecting all terms beyond the first, by making the same assumption as before, namely that $z_i e\psi/kT$ is small compared with unity, it follows that

$$\rho = -\frac{\varepsilon^2\psi}{kT} \sum n_i z_i^2 \quad \dots \quad (xi)^\dagger$$

* It is obvious from equations (i) and (ii), since z_+ and z_- are numerical and do not include the sign of the charge, that n_- is greater than n_+ ; this means that on the average there are more negative than positive ions in the atmosphere around a given positive ion.

† Strictly speaking the values of z_i in equation (x) should include the sign of the charge, but as this becomes z_i^2 in equation (xi) and the sign is immaterial, no change has been made in the symbol. Apart from equation (x), z is always taken as the numerical value, without sign.

The next important step taken by Debye and Hückel was to apply Poisson's equation, thus making the assumption that Coulomb's law is applicable to the electrostatic forces between ions; that is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi\rho}{D} \quad \text{. (xii)}$$

where x , y and z are the rectangular co-ordinates of the given volume element, and D is the dielectric constant of the medium. For brevity equation (xii) is sometimes written in the form

$$\nabla^2 \psi = -\frac{4\pi\rho}{D} \quad \text{(xiiia)}$$

where ∇ represents the appropriate operator. Converting $\nabla^2 \psi$ into polar co-ordinates, and allowing for the fact that the distribution of potential about an ion has spherical symmetry, it can be readily shown that

$$\nabla^2 \psi = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) \quad \text{. (xiiib)}$$

where r , as previously defined, is the distance from a given positive ion of the volume element in which the potential due to the ion is ψ . Substituting the value of ρ from equation (xi) in equation (xiiia), it follows that

$$\nabla^2 \psi = \frac{4\pi e^2}{DkT} \psi \sum n_i z_i^2 \quad \text{. (xiii)}$$

$$= \kappa^2 \psi \quad \text{. (xiv)}$$

where

$$\kappa = \sqrt{\frac{4\pi e^2 \sum n_i z_i^2}{DkT}} \quad \text{. (xv)}$$

Combining equations (xiiib) and (xiv) and integrating, it is found that

$$\psi = \frac{Ae^{-\kappa r}}{r} + \frac{A'e^{\kappa r}}{r} \quad \text{. (xvi)}$$

where A and A' are integration constants. The quantity $1/\kappa$ is often called the thickness of the ionic atmosphere: it has the dimensions of a distance, and is of the order of 10^{-8} cm. for ordinary solutions. If the whole of the charge of the ionic atmosphere, which is of course equal and opposite to that of the given ion, were placed at a distance $1/\kappa$ from the latter, the potential would be the same at the central ion as that due to the distributed atmosphere.

To proceed further it is necessary to evaluate the integration constants in equation (xvi). As r is increased indefinitely ψ must obviously approach zero, and so A' must be zero. For a very dilute solution $\sum n_i$ is almost zero, and hence so also must be κ , and by equation (xvi) the value of ψ reduces to A/r . The potential

in the neighbourhood of any ion must then be due to this ion alone, and if it may be regarded as a point charge the potential, at small distances, is equal to $\pm z_i \epsilon / Dr$, according as the ion is positively or negatively charged. Comparing this with the value obtained from equation (xvi) it follows that A is equal to $\pm z_i \epsilon / D$, and hence

$$\psi = \frac{\pm z_i \epsilon e^{-\kappa r}}{D} \quad \dots \quad (xvii)$$

This equation may be written in the form

$$\psi = \frac{\pm z_i \epsilon}{Dr} + \frac{\mp z_i \epsilon}{Dr} (1 - e^{-\kappa r}) \quad \dots \quad (xviii)$$

in which the first term, as already seen, is equal to the potential at a distance r caused by a given ion when there are no surrounding ions; the other term in the equation therefore represents the potential arising from the unequal distribution of positive and negative charges in the surrounding ion atmosphere. If r is small the expression $(1 - e^{-\kappa r})$ reduces to κr on developing the exponential series, and the potential due to the ion atmosphere reduces to $\mp z_i \epsilon \kappa / D$. Since this holds for small values of r , it may be considered to apply when r is zero, and hence is equal to the potential at the ion itself, produced by the excess of oppositely charged ions in its vicinity; that is

$$\psi_i = \mp \frac{z_i \epsilon \kappa}{D} \quad \dots \quad (xix)$$

According to a familiar theorem in electrostatics * the work required to charge a given body is half the product of the charge and the potential of the body; this may be regarded as being equal to the free energy it possesses in virtue of its electrical charge and its situation in a region of electrical potential. For an ion, of charge $\pm z_i \epsilon$, this electrical free energy must be equal to

$$\frac{1}{2} \left(\pm z_i \epsilon \times \frac{\mp z_i \epsilon \kappa}{D} \right) = \frac{z_i^2 \epsilon^2 \kappa}{2D}$$

The corresponding free energy for 1 gm. ion is obtained by multiplying by the Avogadro number N , and is thus equal to

$$- N z_i^2 \epsilon^2 \kappa / 2D.$$

In order to connect this energy term with the activity coefficient of an ion it is necessary to introduce an equation relating activity and free energy (cf. p. 112). If G represents the free energy of an ion in a given solution, and G_0 is the value in the standard

* See, for example, Starling, *Electricity and Magnetism*, 1929, p. 123.

state, in which the activity of the ion may be taken as unity, it follows that

$$G - G_0 = RT \ln a \quad \dots \quad (\text{xx})$$

where a is the activity of the ion in the given solution. If 1 gm. ion of the particular ion is under consideration, the corresponding partial molar quantities may be used in equation (xx); thus

$$\bar{G} - \bar{G}_0 = RT \ln a \quad \dots \quad (\text{xxa})$$

Replacing the activity (a) by the product of the molar fraction (N) and the activity coefficient (f),* this equation becomes

$$\begin{aligned} \bar{G} - \bar{G}_0 &= RT \ln Nf \quad \dots \quad (\text{xxb}) \\ &= RT \ln N + RT \ln f \quad \dots \quad (\text{xxc}) \end{aligned}$$

If the given solution were ideal the free energy difference could be expressed as

$$\bar{G} - \bar{G}_0 = RT \ln N \quad \dots \quad (\text{xxd})$$

Comparing equations (xxa) and (xxd) it is seen that the difference between the actual free energy per gm. ion and the ideal value is equal to $RT \ln f$, and if this departure from ideal behaviour may be ascribed to the free energy possessed by the ions as a result of their being surrounded by ionic atmospheres, it follows that

$$RT \ln f_i = - \frac{N z_i^2 \varepsilon^2 \kappa}{2D}$$

$$\text{and} \quad \ln f_i = - \frac{N z_i^2 \varepsilon^2 \kappa}{2DRT} \quad (\text{xxi})$$

Substituting for κ (equation xv) there results

$$\ln f_i = - \frac{N \varepsilon^3 z_i^2 \sqrt{\pi \Sigma n_i z_i^2}}{D^{1.5} k^{0.5} T^{1.5} R} \quad \dots \quad (\text{xxia})$$

Since n_i is the number of ions of a particular kind per c.c., it is equal to $N c_i / 1000$, where c_i is the number of gm. ions per litre; also k may be expressed by R/N , and logarithms to the base 10 may be substituted for natural logarithms; hence

$$\lg - \log f_i = \frac{N^2 \varepsilon^3 \sqrt{\pi / 1000}}{2 \cdot 302 R^{1.5}} \cdot \frac{z_i^2 \sqrt{\Sigma c_i z_i^2}}{(DT)^{1.5}} \quad \dots \quad (\text{xxib})$$

The fraction $\frac{N^2 \varepsilon^3 \sqrt{\pi / 1000}}{2 \cdot 302 R^{1.5}}$ is a universal constant which may be replaced by A' , and so

$$\lg - \log f_i = \frac{A' z_i^2 \sqrt{\Sigma c_i z_i^2}}{(DT)^{1.5}} \quad (\text{xxic})$$

* Since the Debye-Hückel theory postulates complete ionization the coefficient f is used instead of γ (see p. 115).

The term $\Sigma c_i z_i^2$ may be regarded as double the 'ionic strength' (μ) of the solution—defined as half the sum of products of the concentration of each ion and the square of its valency; * that is

$$\Sigma c_i z_i^2 = 2\mu$$

$$\therefore -\log f_i = \frac{A' \sqrt{2} z_i^2 \sqrt{\mu}}{(DT)^{1.5}} \quad \text{. (xxii)}$$

For water as solvent D is 87.8 at 0° , and 78.8 at 25° ; substituting these values, and the known values of N (60.6×10^{23}), ϵ (4.774×10^{-10}), R (8.315×10^7), and π , it is found that

$$-\log f_i = 0.487 z_i^2 \sqrt{\mu} \text{ at } 0^\circ \quad \text{. . . (xxiii a)}$$

$$\text{or} \quad 0.505 z_i^2 \sqrt{\mu} \text{ at } 25^\circ \quad \text{. . . (xxiii b)}$$

In deducing these equations it has been assumed that the ion is a point charge having no dimensions; it is necessary, however, to correct for the actual size of the ions. It has been shown† that in order to do so it is necessary to multiply the electrical free energy term by $1/(1 + \kappa a)$, where κ has the same significance as previously, and a is the average 'effective diameter' of the ions; it may be regarded as the mean distance up to which any ion can approach a given ion, and probably includes the dimensions of a sheath of solvent molecules. Hence

$$-\log f_i = \frac{A' \sqrt{2} z_i^2 \sqrt{\mu}}{(DT)^{1.5}} \cdot \frac{1}{1 + \kappa a} \quad \text{. . . (xxiv)}$$

For a given solvent at a definite temperature κ is proportional to $\sqrt{\Sigma n x^2}$, and hence to $\sqrt{\mu}$; substituting A for $A' \sqrt{2}$, it follows that

$$-\log f_i = \frac{z_i^2 A \sqrt{\mu}}{1 + aB \sqrt{\mu}} \quad \text{. . . (xxv)}$$

The quantity B is made up of known constants, and for water it may be evaluated as 3.3×10^7 at ordinary temperatures. Hückel‡ has further considered the effect of the electrical field of an ion in attracting the molecules of the solvent, which are generally of a dipolar nature, so that they orient themselves about the ion; the result is that the solvent molecules tend to displace other ions, to some extent, from the vicinity of any particular ion. This is equivalent to a 'salting-out' effect, and correction for it may be made by allowing for an increase in the dielectric constant of the solvent around the ions by an amount proportional to the ionic

* The original definition of ionic strength (p. 116) involved concentrations expressed in terms of molalities, but in this derivation volume concentrations are concerned.

† Debye and Hückel, *loc. cit.*

‡ *Physikal. Z.*, 1925, 26, 93.

concentration.* The introduction of this correction leads to the equation

$$-\log f_i = \frac{z_i^2 A \sqrt{\mu}}{1 + aB\sqrt{\mu}} - C\mu \quad \text{. . . (xxvi)}$$

As there may be some doubt as to the exact significance of the constant C , it is sometimes regarded as being empirical in nature and is called the 'salting-out constant': the activity coefficient of a non-electrolyte, as measured by its solubility in the presence of salts, is often given by the expression $\log f = C\mu$, and equation (xxvi) reduces to this form when z_i is zero.

The equations considered hitherto give the activity coefficient of a particular ion; for practical purposes, however, it is the mean activity coefficient (f_{\pm}) which is important. For an electrolyte dissociating into two kinds of ions,

$$f_{\pm} = (f_+^{z_+} f_-^{z_-})^{\frac{1}{z_+ + z_-}} \quad \text{. . . (xxvii)}$$

$$\therefore \log f_{\pm} = \frac{z_- \log f_+ + z_+ \log f_-}{z_+ + z_-} \quad \text{. . . (xxviii)}$$

where z_+ and z_- are the valencies, and f_+ and f_- the activity coefficients of positive and negative ions. Hence

$$-\log f_{\pm} = \frac{z_+ z_- A \sqrt{\mu}}{1 + aB\sqrt{\mu}} - C\mu \quad \text{(xxix)}$$

where A and B are constants for the given solvent at a definite temperature, and C and a are constants for the solute. Sometimes a is included with the constant term B , and the equation becomes

$$-\log f_{\pm} = \frac{z_+ z_- A \sqrt{\mu}}{1 + B_1 \sqrt{\mu}} - C\mu \quad \text{(xxx)}$$

Alternatively, by dividing through by the denominator equation (xxx) may be obtained in an approximate form, sometimes called the Debye-Hückel-Brønsted equation (*vide infra*), which may be written

$$-\log f_{\pm} = z_+ z_- A \sqrt{\mu} - C'\mu \quad \text{. . . (xxxxa)}$$

where C' is a constant, approximately equal to $z_+ z_- AB_1 + C$.

It may be seen from equation (xxb) that strictly speaking the activity coefficients given by the above method should be in terms of concentrations expressed in molar fractions: in dilute solutions

* See also, Butler, *J. Physical Chem.*, 1929, 33, 1015; Scatchard, *Physikal. Z.*, 1932, 33, 22. For the bulk of the solution the increase of dielectric constant is a function of the square-root of the concentration (see p. 170).

the values for volume concentrations or molalities are little different, but as a general rule a correction should be applied. To express activity coefficients in terms of molality the quantity

$$\log (1 + 0.001wm\Sigma v)$$

must be added to the expression for $-\log f_{\pm}$, where w is the molecular weight of the solvent and m the molality.*

Equation (xxix) is an expression of the final form of the treatment of Debye and Hückel as applied to strong electrolytes; it attempts to give a quantitative value for the mean activity coefficient of an electrolyte at different ionic strengths. In dilute solution it is clear that the second term on the right-hand side may be neglected, and the resulting form indicates that the activity coefficient decreases with increasing ionic strength; in more concentrated solution the term $C\mu$ will become appreciable and the activity coefficient may increase—as often does happen—beyond unity. In order to test the accuracy of the Debye-Hückel equation it is necessary to know a , the mean ionic diameter, and C for the given electrolyte; † unfortunately there is yet no *a priori* method available by means of which they may be calculated. ‡ Frequently they are determined empirically from experimental observations of the activity coefficient, but the subsequent agreement with the actual data may not be of great significance. In *very dilute solutions*, however, where the equation reduces to the form

$$-\log f_{\pm} = z_+ z_- A \sqrt{\mu} \quad \text{.} \quad (\text{xxx})$$

it may be unequivocally verified. For an electrolyte in water at 25°, the limiting equation approached at high dilution should be

$$-\log f_{\pm} = 0.505 z_+ z_- \sqrt{\mu} \quad \text{.} \quad (\text{xxxii})$$

The Osmotic Coefficient—The Debye-Hückel limiting equation may be written in another form involving the osmotic coefficient. Bjerrum § has developed thermodynamically a relation which may be written

$$\phi + c \frac{d\phi}{dc} = 1 + c \frac{d \ln f_{\pm}}{dc} \quad (\text{xxxiii})$$

for dilute solutions, where ϕ the osmotic coefficient is equal to i the van 't Hoff factor divided by the number of ions produced by a molecule of electrolyte. || Substituting the limiting value of $\ln f_{\pm}$

* Scatchard, *J. Amer. Chem. Soc.*, 1925, 47, 2098.

† A and B are constants for the solvent, and are known.

‡ See, however, La Mer and Goldman, *ibid.*, 1931, 53, 473; Crockford *et al.*, *ibid.*, 1933, 55, 568; 1936, 58, 87, for attempts to correlate a with other properties.

§ *Z. Elektrochem.*, 1918, 24, 321; *Z. physikal. Chem.*, 1923, 104, 406.

|| The quantity of $1 - \phi$ is the same as j defined on p. 117.

as obtained from the Debye-Hückel equation and integrating, it is found that

$$1 - \phi = -\frac{1}{2} \ln f_{\pm} \quad (\text{xxxiva})$$

$$\therefore 1 - \phi = \frac{2 \cdot 302}{3} \cdot 0.505 z_+ z_- \sqrt{\mu} \text{ at } 25^\circ \quad (\text{xxxivb})$$

$$= 0.387 z_+ z_- \sqrt{\mu} \text{ at } 25^\circ \quad (\text{xxxva})$$

$$\text{or} \quad 0.376 z_+ z_- \sqrt{\mu} \text{ at } 0^\circ \quad (\text{xxxvb})^*$$

Tests of the Debye-Hückel Theory—General—The equations developed from the Debye-Hückel theory may be tested by measurements of various kinds; since the theory was introduced a great deal of work has been carried out in this connection. It is interesting to note that the simple Debye-Hückel equation (xxxi) is in agreement with the empirical conclusion of Lewis and Randall (see pp. 116, 120 *supra*) that the activity of an electrolyte is the same in all solutions of the same ionic strength. In addition Lewis and Linhart † had suggested a formula for a strong electrolyte (cf. p. 118), which may be written as

$$1 - \phi = \beta c^\alpha$$

where α was about 0.5, and β depended on the valency type of the salt; this equation is of the same type as the limiting Debye-Hückel equation. Further, Brønsted ‡ found empirically that the equations

$$1 - \phi = 0.32 \sqrt{c}$$

$$\text{and} \quad \log f_{\pm} = -0.42 \sqrt{c}$$

were in agreement with observations; these only differ from the Debye-Hückel formulæ in the values of the constants, which Brønsted and La Mer § have shown to be liable to error as they were based on measurements in very dilute solutions. Brønsted's extended formula || for uni-univalent electrolytes

$$\log f_{\pm} = -0.42 \sqrt{c} + ac$$

is in general agreement with equation (xxxa) which should hold for more concentrated solutions. For a series of electrolytes of the same valency type, with approximately constant ionic diameters, it follows from the extended form of the Debye-Hückel equation that

$$\log f/f_R = k_c$$

where f/f_R is the ratio of the activity coefficient of any electrolyte to that of a reference substance of the same valency type at the concen-

* For alternative derivation, see Cantelo, *J. Physical Chem.*, 1929, 33, 627.

† *J. Amer. Chem. Soc.*, 1919, 41, 1951.

‡ *Ibid.*, 1922, 44, 938.

§ *Ibid.*, 1924, 46, 555.

|| Brønsted and La Mer, *loc. cit.*; Scatchard, *ibid.*, 1925, 47, 641.

tration c , and k is a constant for the given electrolyte. This relationship has been confirmed for a large number of uni-univalent compounds over a considerable range of concentration.*

Solubility—It has already been proved that the solubility of a salt in any solution not containing a common ion is inversely proportional to the mean activity coefficient of the salt in the given solution (p. 128). If S_0 is the solubility in pure water, S the value in the presence of other electrolytes, and $f_{0\pm}$ and f_{\pm} the mean activity coefficients in the two solutions, then

$$\frac{S}{S_0} = \frac{f_{0\pm}}{f_{\pm}} \text{ and } \log \frac{S}{S_0} = \log f_{0\pm} - \log f_{\pm} \quad (\text{xxxvi})$$

According to the Debye-Hückel theory, for dilute solutions,

$$-\log f_{0\pm} = Az_+z_- \sqrt{\mu_0}$$

and

$$-\log f_{\pm} = Az_+z_- \sqrt{\mu},$$

where μ_0 and μ represent the ionic strengths of the solutions containing the salt only and one containing added salts, respectively. It follows, therefore, that

$$\log \frac{S}{S_0} = Az_+z_-(\sqrt{\mu} - \sqrt{\mu_0}) \quad (\text{xxxvii})$$

From this equation it may be seen that if $\log S/S_0$ is plotted against $\sqrt{\mu}$ for a given saturating salt ($\mu_0 = \text{constant}$), the limiting slope of the curve in dilute solutions should be Az_+z_- , irrespective of the nature of the salts added. This has been tested by means of new and old experimental data for solubility measurements in water at ordinary temperatures and at 75° ($D = 63.7$), in acetone ($D = 21$), in methyl alcohol ($D = 30$), in mixtures of water and ethyl alcohol ($D = 78.8$ to 33.8), in acetic acid ($D = 6.25$) and in ethylene dichloride ($D = 10.4$).†

The slope of the curve has been found to be proportional to the product of the valencies of the saturating salt (z_+z_-), as required by the theory, but the value of A is sometimes different from that to be expected theoretically. This may, in some cases, be due to

* Åkerlöf and Thomas (H. C.), *ibid.*, 1934, 56, 593.

† Brønsted and La Mer, *loc. cit.*; Noyes, *J. Amer. Chem. Soc.*, 1924, 46, 1098; Brønsted and Brumbaugh, *ibid.*, 1926, 48, 2015; Baxter, *ibid.*, p. 626; La Mer *et al.*, *ibid.*, 1927, 49, 363, 410; Robinson (A. L.), *J. Physical Chem.*, 1928, 32, 1089; Williams (J. W.), *J. Amer. Chem. Soc.*, 1929, 51, 1112; 1930, 52, 2759; Brønsted *et al.*, *Z. physikal. Chem.*, 1928, 134, 97; 1932, 162, 128; Larsson and Adell, *Z. anorg. Chem.*, 1931, 196, 354; Peterson and Myers, *J. Amer. Chem. Soc.*, 1930, 52, 4853; MacDougall (F. H.), *ibid.*, p. 1390; 1934, 56, 368; Neuman, *ibid.*, 1932, 54, 2195; Scholl, Hutchison and Chandlee, *ibid.*, 1933, 55, 3081; Seward, *ibid.*, 1934, 56, 2610; MacDougall (G.) and Davies, *J. Chem. Soc.*, 1935, 1416.

incomplete dissociation of the electrolytes present.* Considerable deviations from the theoretical curve have been observed when the saturating salt has an ion of high valency, and the added salts have high valency ions of opposite sign; for example the solubility of lanthanum iodate is abnormal in the presence of sulphates, although the results with chlorides and nitrates present are in agreement with the Debye-Hückel theory.† These deviations are probably to be ascribed, to some extent at least, to the neglect of certain terms (see p. 138) in the development of the original equation for the activity coefficient; this aspect of the subject will be considered shortly. The deviations resulting from this neglect are more marked the higher the valency of the ions and the lower the dielectric constant of the medium. Other possible causes of deviation from theoretical behaviour are the neglect of ionic size in the limiting Debye-Hückel equation and the formation of chemically solvated ions.‡

Osmotic Properties—Hovorka and Rodebush§ have determined the freezing-point depressions given by salts of various valency types; the results, as well as those quoted by Debye and Hückel in their original papers, are in excellent agreement with the limiting form of the Debye-Hückel equation. In more concentrated solutions it was found necessary to apply the correction for the size of the ions, and when values of the order of $1 - 3 \times 10^{-8}$ cms. were used the agreement between observed and calculated freezing-point depressions was very good. On the other hand Randall and Vanselow|| determined the activity coefficients of hydrochloric acid, thallic chloride and lead nitrate from freezing-point measurements; it was found that although the limiting equation was of the form $\log f_{\pm} = -Az_{+}z_{-}\sqrt{\mu}$, the value of A for water at 0° was 0.39 to 0.46, rather than 0.487 required by the theory. Scatchard,** however, has noted that by allowing for the size of the ions the results may be made to comply excellently with the extended Debye-Hückel equation. The freezing-point measurements in aqueous solutions collected by Noyes,†† by Randall and Scott‡‡ and

* See Davies, *ibid.*, 1930, 2410; Macdougall and Davies, *loc. cit.*

† La Mer and Mason, *loc. cit.*; La Mer and Cook, *J. Amer. Chem. Soc.*, 1929, 51, 2622; La Mer and Goldman, *ibid.*, p. 2632. The 'specific interaction principle' of Brønsted (see p. 127) still holds; see, however, Davies, *loc. cit.*

‡ For solubility data showing the limitations of the Debye-Hückel treatment, see Schärer, *Physikal. Z.*, 1924, 25, 145; Partington *et al.*, *Trans. Faraday Soc.*, 1928, 24, 518; 1930, 26, 78; 1934, 30, 619; Kraus and Seward, *ibid.*, 1927, 23, 488; *J. Physical Chem.*, 1928, 32, 1294; Seward and Schumb, *J. Amer. Chem. Soc.*, 1930, 52, 3962; Neuman, *ibid.*, 1933, 55, 879; Chloupek *et al.*, *Coll. Czech. Chem. Comm.*, 1933, 5, 21.

§ *J. Amer. Chem. Soc.*, 1925, 47, 1614. || *Ibid.*, 1924, 46, 2418.

** *Ibid.*, 1925, 47, 641. †† *loc. cit.* ‡‡ *Ibid.*, 1927, 49, 647.

by Scatchard and Prentiss * appear to be in general agreement with theoretical requirements. Activity coefficients determined from vapour pressure measurements † at 25° and from the elevation of the boiling point of water ‡ ($D = 55.3$ at 100°) also bear out the inter-ionic attraction theory. Osmotic effects in non-aqueous solutions are also in general agreement with the Debye-Hückel equations; freezing-point determinations made in such divergent solvents as liquid ammonia (f.pt. -75° , $D = 25.1$), acetic acid (f.pt. 16.6° , $D = 7$) and cyclohexanol (f.pt. 24° , $D = 15$), and boiling-point elevations in methyl and ethyl alcohols ($D = 22.7$ and 18.7 respectively) and in acetone ($D = 21$), all comply with the theory.§ Some measurements in acetic acid solution are apparently not in harmony with it, but the discrepancy may possibly be due to incomplete dissociation in a medium of such low dielectric constant.||

E.M.F. Measurements—The activity coefficients of various electrolytes calculated from *E.M.F.* measurements are in general agreement with the equation $-\log f_{\pm} = z_+ z_- A \sqrt{\mu}$ in dilute solutions, but the value of A , particularly in non-aqueous solutions, was at one time thought to be smaller than the theoretical value. Thus Noyes and Baxter ** found A to be 0.7 times that expected for aqueous and aqueous alcoholic solutions of hydrochloric acid and sodium and lithium chlorides; similar results were obtained by Nonhebel and Hartley.†† It is now generally agreed, however, that the difference is due to experimental errors or to other factors. The limiting slope of the plot of $-\log f_{\pm}$ against $\sqrt{\mu}$, which should be related to A , is greater than the expected value for aqueous solutions of sulphuric acid, but the discrepancy disappears when an allowance is included for partial dissociation of the bisulphate ion.‡‡ Measurements of *E.M.F.*'s made in aqueous solutions of simple salts and acids, in aqueous glycerol and sucrose solutions, in acetic acid and in mixtures of water with methyl or ethyl alcohol yield

* *Chem. Reviews*, 1933, 13, 139; see also Lange (J.), *Z. Elektrochem.*, 1933, 39, 545; *Z. physikal. Chem.*, 1934, 168, 147.

† Robinson (R. A.), *J. Amer. Chem. Soc.*, 1935, 57, 1161, 1165.

‡ Saxton and Smith (R. P.), *ibid.*, 1932, 54, 2626.

§ Webb, *ibid.*, 1926, 48, 2263; Schreiner and Frivold, *Z. physikal. Chem.*, 1926, 124, 1; Frivold, *J. Physical Chem.*, 1926, 30, 1153; Robinson (A. L.), *ibid.*, 1929, 33, 1193; Schreiner, Frivold and Ender, *Phil. Mag.*, 1929, 8, 669.

|| Eichelberger, *J. Amer. Chem. Soc.*, 1934, 56, 799.

** *ibid.*, 1925, 47, 2122.

†† *Phil. Mag.*, 1925, 50, 729; 1926, 2, 1085; see, however, Scatchard, *ibid.*, 1926, 2, 577.

‡‡ Shrawder and Cowperthwaite, *J. Amer. Chem. Soc.*, 1934, 56, 2340; see also, *ibid.*, p. 544; and Scatchard and Tefft, *ibid.*, 1930, 52, 2272, for other cases.

activity coefficients in accordance with the requirements of the Debye-Hückel theory.*

Thermal Properties of Electrolytes—It has been already seen that the energy required to charge 1 gm. ion of a particular kind of ion in a given solution is $-Nz_i^2\epsilon^2\kappa/2D$, and for 1 gm. mol. of electrolyte the corresponding energy term is $-\sum N\nu_i z_i^2\epsilon^2\kappa/2D$, where ν_i is the number of ions of the i th kind resulting from the ionization of one molecule of the solute. The electrical work required to separate the ions of 1 gm. mol. of salt to an infinite distance from one another (ΔW), which is equivalent to the free energy of diluting the given solution to infinity, is equal to two-thirds of the energy of charging; † hence

$$-\Delta W = -\sum N\nu_i z_i^2\epsilon^2\kappa/3D \quad \dots \quad (\text{xxviii})$$

In order to obtain the 'integral heat of dilution' (ΔU), defined as the heat evolved when a solution at a particular concentration is mixed isothermally with an infinite bulk of solvent, ‡ it is only necessary to apply the Gibbs-Helmholtz equation in the form

$$\Delta U = -T^2 d(\Delta W/T)/dT \quad \dots \quad (\text{xxix})$$

Carrying out the differentiation at constant volume, that is n_i in the expression for κ (equation xv) is constant, and noting that both D and T are involved in the latter, it is seen § that

$$\Delta U = \frac{\sum N\nu_i z_i^2\epsilon^2\kappa}{2D} \left[1 + \frac{T}{D} \left(\frac{dD}{dT} \right)_v \right] \quad (\text{xl})$$

In actual practice the heat of dilution (ΔH) is measured at constant

* Scatchard, *ibid.*, 1925, 47, 641; 1926, 48, 2026; 1930, 52, 2272; Harned *et al.*, *ibid.*, 1926, 48, 1160, 3095; 1930, 52, 5079; 1932, 54, 423; 1933, 55, 2179; 1936, 58, 761, 989; *J. Physical Chem.*, 1926, 30, 1585; *Physikal. Z.*, 1926, 121, 254; Güntelberg, *Z. physikal. Chem.*, 1926, 123, 199; Lucasse, *ibid.*, 1926, 121, 254; *J. Amer. Chem. Soc.*, 1926, 48, 626; Bray, *ibid.*, 1927, 49, 2372; Brester, *Rec. trav. chim.*, 1927, 46, 328; Millet, *Trans. Faraday Soc.*, 1929, 25, 147; Butler and Robertson (C. M.), *Proc. Roy. Soc.*, 1929, 125 A, 694; Åkerlöf, *J. Amer. Chem. Soc.*, 1930, 52, 2353; Quintin, *Compt. rend.*, 1931, 193, 846; Chloupek *et al.*, *Coll. Czech. Chem. Comm.*, 1932, 4, 124, 165; MacDougall (F. H.) and Blumer, *J. Amer. Chem. Soc.*, 1933, 55, 2236; Gelbach, *ibid.*, p. 4857; Cowperthwaite, La Mer and Barksdale, *ibid.*, 1934, 56, 544; Tippetts and Newton, *ibid.*, p. 1675; Brown (A. S.) and MacInnes, *ibid.*, 1935, 57, 1356; Keston, *ibid.*, p. 1462; Scholl, Hutchison and Chandlee, *ibid.*, p. 2542.

† Debye, *Physikal. Z.*, 1924, 25, 97; see also, Noyes, *J. Amer. Chem. Soc.*, 1924, 46, 1080; Adams (E. Q.), *ibid.*, 1926, 48, 621; Fuoss, *J. Chem. Physics*, 1934, 2, 818.

‡ The integral heat of dilution is the difference between the heat of solution of the electrolyte at the given concentration and at infinite dilution.

§ Gross (P.) and Halpern, *Physikal. Z.*, 1925, 26, 403; Bjerrum, *Z. physikal. Chem.*, 1926, 119, 145.

pressure, and so also is dD/dT , the temperature coefficient of the dielectric constant, and hence it is necessary to apply a correction to equation (xl): this involves the inclusion of the term $(dV/dT)_p T/3V$, where V is the volume, in the square bracket.* The differential $(dV/dT)_p$ is, of course, the coefficient of thermal expansion of the solution. For dilute solutions the error involved in the neglect of this correction is generally quite small, and the fact that it was ignored in earlier work is not serious, especially as the correction is probably not greater than the relatively large experimental error. By inserting the known values for the various constants and the temperature coefficient of the dielectric constant, unfortunately not known very accurately, in equation (xl), the integral heat of dilution of *any* uni-univalent strong electrolyte should be, approximately,

$$\Delta H = -480\sqrt{c} \quad \dots \dots \dots (xli)$$

at 25°, where c is the initial concentration of the solution.

A striking point about this result is that it requires there should be a decrease of heat content on dilution,† that is heat should be *evolved* in the process: this important consequence of the inter-ionic attraction theory at first appeared to be contrary to experimental observation, but later work has shown that for solutions more dilute than 0.1*N* the integral heat of dilution is positive for most electrolytes. According to the theory ΔH should be a linear function of \sqrt{c} , and there is no doubt, as a result of the comprehensive investigations of Lange (E.) and his collaborators, and of others,‡ with a large number of salts that this is the case for dilute solutions, generally up to 0.01*N*. The slope of the line should be 480, for all uni-univalent salts, but it is only with lithium fluoride that this is nearly the case. It may be noted that owing to hydration both lithium and fluorine ions are larger than any other simple univalent ions in aqueous solution: the significance of this fact will appear shortly. For concentrated solutions allowance has to be made for the mean ionic diameter a , as in the Debye-Hückel treatment. By introducing the $1/(1 + \kappa a)$ factor, as in the calculation of the activity coefficient, and giving a reasonable values, of the order of 3 to 5 Å, a satisfactory agreement can be obtained between experi-

* Gatty, *Phil. Mag.*, 1931, 11, 1082; 1934, 18, 46; Scatchard, *J. Amer. Chem. Soc.*, 1931, 53, 2037.

† This is due to the fact that dD/dT is negative.

‡ *Z. Elektrochem.*, 1927, 33, 439; 1928, 34, 566; 1930, 36, 772; *Physikal. Z.*, 1928, 29, 760; 1929, 30, 670; *Z. physikal. Chem.*, 1930, 149, 51; 1931, 157, 1; 1932, 160, 445; 1933, 165, 89; 1934, 169, 103; *J. Amer. Chem. Soc.*, 1930, 52, 4218; 1933, 55, 4733; Richards (T. W.) and Dole, *ibid.*, 1929, 51, 794; Robinson (A. L.) *et al.*, *ibid.*, 1932, 54, 1311, 3120; 1934, 56, 2312; Gatty, Wolfenden *et al.*, *J. Chem. Soc.*, 1934, 1376. For review, see Lange and Robinson, *Chem. Reviews*, 1931, 9, 89.

mental and theoretical results at appreciable concentrations. There are, however, still some discrepancies, depending on the individual nature of the salt, which require explanation. Such factors as the dependence of the effective ionic diameter on temperature, uncertainty concerning the temperature coefficient of dielectric constant in the solution, incomplete dissociation and ion-solvent complex formation may account for the deviations. From equation (xl) it can be shown that the integral heats of dilution of two electrolytes of different valency types at the same concentration should differ only in the factor $(\sum v_i z_i^2)^{1.5}$. The ratio of these heats for a uni-univalent and a uni-bivalent (or bi-univalent) salt should thus be 1 to $3^{1.5}$, that is 1 to 5.2; experimentally a ratio in dilute solution of approximately 1 to 4.5 has been found. This agreement is satisfactory, especially as the 1-2 and 2-1 valency types of electrolytes show departures from theoretical behaviour at quite low concentrations. The integral heats of dilution provide an exceptionally sensitive test for the inter-ionic attraction theory and on the whole the experimental results may be said to support the theory: * in non-aqueous solutions, however, there are some discrepancies which have yet to be explained.†

The relative partial molar heat content is related to the integral heat of dilution, and can be obtained directly from it by a process involving differentiation with respect to temperature,‡ or it can be calculated from *E.M.F.* measurements of concentration cells at various temperatures § (cf. Chapter XIII): according to the inter-ionic attraction theory of strong electrolytes it should also be a linear function of \sqrt{c} . Similarly, the relative partial specific heat can be calculated theoretically, a double differentiation of the electrical free energy with respect to temperature being involved, or it can be determined from thermochemical or *E.M.F.* measurements ||; this quantity should also depend on \sqrt{c} in a linear manner. From the experimental data, it is clear that the thermal quantities are linear functions of \sqrt{c} , but the slopes of the lines are often appreciably different from those expected theoretically.** In this work, how-

* See, however, Plake, *Z. physikal. Chem.*, 1932, 162, 257.

† Gatty, Wolfenden *et al.*, *loc. cit.*

‡ Rossini, *Bur. Stand. J. Res.*, 1931, 6, 791; Robinson (A. L.), *J. Amer. Chem. Soc.*, 1932, 54, 1311; 1934, 56, 2637.

§ La Mer *et al.*, *ibid.*, 1933, 55, 1004, 4343; Cowperthwaite and Shrawder, *ibid.*, 1934, 56, 2345; Harned *et al.*, *ibid.*, 1933, 55, 2179; 1934, 56, 650, 4838; 1935, 57, 27; 1936, 58, 761.

|| Randall and Rossini, *ibid.*, 1929, 51, 323; Robinson *loc. cit.*; La Mer *et al.*, *loc. cit.*; Harned *et al.*, *loc. cit.*; Hammerschmid and Lange (E.), *Z. physikal. Chem.*, 1932, 160, 445.

** See also, Gucker *et al.*, *J. Amer. Chem. Soc.*, 1932, 54, 1358; 1933, 55, 1013; 1935, 57, 78; Young (T. F.) and Groenier, *ibid.*, 1936, 58, 187.

ever, experimental errors cause considerable deviations and the necessary data for the theoretical calculations, such as the values of d^2D/dT^2 and d^2V/dT^2 , are not known with any certainty.

Other Properties of Solutions—The apparent molar volume of a solute, which is related to the density of the solution, and the molar compressibility and apparent thermal expansibility of an electrolyte are connected with its electrical free energy, the first of these being obtainable by differentiation with respect to pressure,* the second by double differentiation,† and the last by successive differentiation with respect to pressure and temperature.‡ The apparent molar volume of the solute (ϕ) is directly determinable from experimental data, and according to the Debye-Hückel treatment of inter-ionic attraction as applied to the theory of complete ionization of strong electrolytes, the equation

$$\phi = \phi_0 + \Sigma(v_i z_i^2)^{1.5} A \sqrt{c} \quad . \quad . \quad . \quad (xlii)$$

where ϕ_0 is equivalent to the apparent molar volume at infinite dilution, and A is a calculated constant, should apply. From density measurements in water and in methyl alcohol it has been confirmed that the apparent molar volume varies in a linear manner with the square-root of the concentration; the slopes of the curves are in satisfactory agreement with the theoretical requirements, both as regards the value of A and the valency factor preceding it in equation (xlii), in dilute solutions.§ It is somewhat surprising that the linear relationship between ϕ and \sqrt{c} extends apparently to high concentrations of the electrolyte, but the slopes of the curves under these conditions differ from those to be expected theoretically.|| According to the inter-ionic attraction theory the molar compressibility and thermal expansibility should also be linear functions of \sqrt{c} , and the slopes of the curves should depend on the valency type of the electrolyte. Only a limited number of observations of these properties have hitherto been made, but the results are in general agreement with theory.** It has been stated that the apparent molar volumes and compressibilities of solutions of the non-elec-

* Redlich, *Naturwiss.*, 1931, 19, 251; Redlich and Rosenfeld, *Z. physikal. Chem.*, 1931, 155, 65.

† Gucker, *Chem. Reviews*, 1933, 13, 111; contains a review of the apparent molar properties of electrolytes.

‡ *Idem.*, *J. Amer. Chem. Soc.*, 1934, 56, 1017.

§ Redlich and Rosenfeld, *loc. cit.*; *Z. Elektrochem.*, 1931, 37, 705; Geffcken, *Z. physikal. Chem.*, 1931, 155, 1; 1934, B 26, 81; Vosburgh, Connell and Butler, *J. Chem. Soc.*, 1933, 933; Cantelo and Phifer, *J. Amer. Chem. Soc.*, 1933, 55, 1333; Gucker, *Chem. Reviews*, 1933, 13, 111.

|| Masson, *Phil. Mag.*, 1929, 8, 218; Scott, *J. Physical Chem.*, 1931, 35, 2315, 3379; 1932, 36, 1022; 1934, 38, 951.

** Gucker, *loc. cit.*; *J. Amer. Chem. Soc.*, 1933, 55, 2709; see also Gibson, *ibid.*, 1935, 57, 284.

trolytes sucrose and urea also vary linearly with the square-root of the concentration, and so the results for electrolytes can only be regarded as significant if the slopes of the lines are close to the theoretical values.*

Debye-Hückel and Milner Theories—When comparing the Milner theory with that of Debye and Hückel, it was shown by Noyes † that the limiting forms of both equations for a uni-univalent electrolyte could be reduced to the type $-\log f = A\sqrt{\mu}$, but the value of A in the Milner equation was 0.7 times that deduced from the Debye-Hückel theory. It has been seen that many of the first experimental tests of the theory indicated that A was actually less than the value given by equation (xxii), and so it appeared that the results were in better agreement with Milner's treatment. Since both theories involve the same fundamental assumptions, and differ only in their mathematical treatment, they should lead to the same conclusions; the discrepancy may be due to the approximations used by Milner in developing the numerical value for the virial, but more probably to a slight confusion in terms, as pointed out by Adams (E. Q.).‡ Rectifying the error made by Milner in this connection, his equation becomes almost identical with that of Debye and Hückel, and the two theories must be regarded as equivalent; they differ only in the method of treatment for evaluating the inter-ionic forces. Support for this view is provided by the increasing evidence for the correctness of the A constant in the Debye-Hückel equation.§

Extension of the Debye-Hückel Treatment—In the calculation of the electric density near an ion, all terms beyond the first were neglected by Debye and Hückel in the expansion of an exponential series (cf. equation viii). It was assumed that $z_i e \psi / kT$ was small, and this implies that the mutual potential energy of two ions at their distance of closest approach, that is when they are separated by a , the effective diameter of the ions (p. 142), is small compared with their mean thermal energy of translation.¶ To avoid this approximation, which becomes hardly justifiable with ions of high valency and large size and with solvents of low dielectric constant, H. Müller ** adopted a graphical method, but a more useful procedure was devised by Gronwall, La Mer and Sandved †† who

* See, however, Falkenhagen and Bachem, *Z. Elektrochem.*, 1935, **41**, 570.

† *J. Amer. Chem. Soc.*, 1924, **46**, 1080. ‡ *Ibid.*, 1926, **48**, 621.

§ MacInnes and Shedlovsky, *ibid.*, 1931, **53**, 2419; Hall (N. F.), *ibid.*, 1932, **54**, 831; Davies, *ibid.*, p. 1698; and other references *supra*.

¶ See Fowler, *Trans. Faraday Soc.*, 1927, **23**, 434.

** *Physikal. Z.*, 1927, **28**, 324; 1928, **29**, 78.

†† *Ibid.*, 1928, **29**, 358; for the treatment of salts of unsymmetrical valency type, see La Mer, Gronwall and Greiff, *J. Physical Chem.*, 1931, **35**, 2345.

used the complete expansion for the electric density, followed by approximate integration of the Poisson equation in the form of a power series. In this manner the activity coefficient of a symmetrical electrolyte, that is one having both ions of the same valency (z), is given by the expression

$$\ln f_{\pm} = - \frac{Nz^2 \epsilon^2 \kappa}{2DRT} \cdot \frac{1}{1 + \kappa a} + \sum_{-1} \left(\frac{Nz^2 \epsilon^2}{DRTa} \right)^{2m+1} \left[\frac{1}{2} X_{2m+1}(\kappa a) - 2m Y_{2m+1}(\kappa a) \right] \quad (\text{xliii})$$

where $X(\kappa a)$ and $Y(\kappa a)$ are known functions of κa , which have been evaluated and recorded in tables; the other symbols in equation (xliii) have the same significance as previously. It will be noted, by comparing this equation with equations (xxi) and (xxiv), that the first term is identical with the Debye-Hückel equation with correction for ionic size, and that the second term is in the form of a series. Strictly speaking the latter should be summed for all integral values of m from 1 to infinity, but it is found that successive terms in the series decrease rapidly as m increases, and it is only necessary, in general, to include two terms. These additional terms, which must be added to the one required by the simple Debye-Hückel theory, are negligible in aqueous solution if a/z^2 is greater than about 1.5×10^{-8} cm., that is for a uni-univalent salt if a is greater than 1.5 Å, but for a bi-bivalent type only if it exceeds 6 Å. Since the effective diameters of most ions is greater than 1.5 Å but less than 6 Å, the first approximation of Debye and Hückel is found to apply for uni-univalent electrolytes, but it breaks down when the ions have a higher valency. For solvents of lower dielectric constant the Gronwall-La Mer additional terms become negligible at larger ionic diameters than is the case with water, and so deviations from the Debye-Hückel equation are more marked.

In the application of equation (xliii) an arbitrary value of a is chosen so as to give a calculated mean activity coefficient which agrees with that found experimentally, and the test of the equation is that the a values at a number of different concentrations should not only be of reasonable magnitude but almost constant. There is little doubt that the Gronwall-La Mer extension represents an important advance over the simple Debye-Hückel treatment: in many instances where the latter requires impossible, e.g. negative, values of a , which vary markedly with concentration, those required for equation (xliii) are constant and of the correct magnitude. The equation has been tested by means of solubility, *E.M.F.*, and osmotic data,* with very satisfactory results, and it appears that but for the

* Gronwall, La Mer *et al.*, *loc. cit.*; La Mer *et al.*, *J. Physical Chem.*, 1931, 35, 1953; 1936, 40, 287; *J. Amer. Chem. Soc.*, 1931, 53, 2040,

tedious nature of the calculation equation (xliii) would be more widely used.

The Ion-Association Treatment—An alternative, somewhat more physical, method for allowing for the fact that the Debye-Hückel approximation is justified if the distance of closest approach of the ions is greater than a certain value was used by Bjerrum.* The probability that any ion will be within a distance r of an ion of opposite sign can be calculated mathematically, and it has been found that this probability has a minimum value, given by

$$r_{\min.} = \varepsilon^2 z_i z_j / 2 D k T \quad (\text{xliv})$$

where z_i and z_j are the valencies of the ions of opposite sign. According to Bjerrum, if the sum of the radii of the ions exceeds $r_{\min.}$ then the Debye-Hückel approximation may be regarded as applicable, but when the sum is less than this value the ions may be regarded as being associated in pairs, in which state they contribute nothing to the electrical free energy if they have the same valency. It should be made clear that the distinction between the associated 'ion-pairs' and free ions is a purely arbitrary one, and that no real physical or chemical significance is to be applied to it, as has sometimes been done. By assuming that the law of mass action is applicable to the equilibrium between free and associated ions, an assumption which is thermodynamically justifiable, Bjerrum deduced a relationship of the form

$$1/K = \frac{4\pi N}{1000} \left(\frac{\varepsilon^2}{D k T} \right)^3 Q(b) \quad (\text{xlv})$$

where K is the equilibrium constant of the system



and $Q(b)$ is a function of the effective ionic diameter (a) or distance of closest approach of oppositely charged ions. By a process of trial and error, the value of a necessary to give the correct electrical free energy, and hence of the activity coefficient of an electrolyte, is found, on the assumption that free ions only contribute to the electrical energy. In this way, Bjerrum showed that in a number of cases where the simple Debye-Hückel treatment led to impos-

4333; 1932, 54, 2763; 1934, 56, 544; Seward *et al.*, *ibid.*, 1930, 52, 3962; 1932, 54, 554; Neuman, *ibid.*, p. 2195; Harned and Ehlers, *ibid.*, 1933, 55, 2179; Heston and Hall (N. F.), *ibid.*, 1934, 56, 1462; Scholl, Hutchison and Chandless, *ibid.*, 1935, 57, 2542; Lebetre, *J. Chim. physique*, 1934, 31, 348; Partington *et al.*, *Trans. Faraday Soc.*, 1934, 30, 1134; *Phil. Mag.*, 1936, 22, 857. For the Gronwall-La Mer treatment applied to heats of dilution, see Lange and Meixner, *Physikal. Z.*, 1929, 30, 670; Scatchard, *J. Amer. Chem. Soc.*, 1931, 53, 2037.

* *Kgl. Danske Videnskabs. Selsk. Math.-fys. Medd.*, 1926, 1, [9], 1.

sible results for the mean ionic diameter the ion-association procedure gave reasonable values.

For several years the Bjerrum method, apart from a qualitative application which will be mentioned shortly, found little application,* but since 1933 it has been developed by Fuoss and Kraus † and applied by them especially in connection with conductivity measurements in media of low dielectric constant. The dissociation constants for the equilibrium between associated and free ions were calculated from the data, by a method to be considered later (p. 165), and from these the effective ionic diameters of various electrolytes were evaluated with the aid of equation (xlv): the results obtained provide strong support for the views upon which the calculations were based. The variation of the dissociation constant for a given salt with the dielectric constant of the solvent has also been verified from conductance data in a series of dioxan-water mixtures. ‡ The concept of ion-association in pairs has been extended to the possibility of the formation of 'triplet-ions' in media of low dielectric constant: reference to this aspect of the subject will be made subsequently.

An examination of equation (xlv) shows that $r_{\min.}$ is larger, the larger the valencies of the ions and the lower the dielectric constant of the medium: for relatively small ions the departure from the ideal Debye-Hückel behaviour will, therefore, be more marked under these conditions. This is in harmony with experience and with the conclusions reached from the Gronwall-La Mer treatment. For water at 25°, $r_{\min.}$ is 3.5 Å for a uni-univalent salt: if the sum of the ionic radii exceeds this value then all the ions may be supposed to be free and the Debye-Hückel approximation applicable. The agreement with the Gronwall-La Mer extension is, therefore, only of a qualitative nature, although both treatments imply that the simple equations derived from the inter-ionic attraction theory should be satisfactory for relatively large ions.

Discussion—Several authors § have made a critical examination of the theoretical bases underlying the arguments described in this chapter, and although it is agreed that the Debye-Hückel equation

* See, however, Scatchard and Tefft, *J. Amer. Chem. Soc.*, 1930, 52, 2272.

† *Ibid.*, 1933, 55, 1019, 2387, 2776, 3537, 3609; 1935, 57, 2604; 1936, 58, 255; *Trans. Faraday Soc.*, 1934, 30, 967; 1935, 31, 749; 1936, 52, 594; for reviews, see Kraus, *Trans. Amer. Electrochem. Soc.*, 1934, 66, 385; Fuoss, *Z. Elektrochem.*, 1933, 39, 513; *Chem. Reviews*, 1935, 17, 27.

‡ Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, 55, 1019.

§ Fowler, *loc. cit.*; Kramers, *Proc. K. Akad. Wetensch. Amsterdam*, 1927, 30, 145; Onsager, *Chem. Reviews*, 1933, 13, 73; Halpern, *J. Chem. Physics*, 1934, 2, 85; Kirkwood, *ibid.*, p. 767; Fuoss, *ibid.*, p. 818; Guggenheim, *Phil. Mag.* 1935, 19, 589.

is justifiable as a limiting law applicable at infinite dilution, there is some doubt about the situation in connection with real solutions. The chief uncertainty lies in the application of the Boltzmann-Poisson equations to electrolytes: this is only satisfactory provided the potential at a given ion due to its ionic atmosphere is proportional to the charge on the ion. From equation (xix) it is evident that this is the case in the simple Debye-Hückel treatment, but if allowance is made for the additional terms in equation (viii), as was done by Gronwall, La Mer and Sandved,* and by Müller (H.),† then the necessary condition for the Boltzmann-Poisson principle no longer holds! It appears from this argument that the Bjerrum treatment, in which the simplified equation (ix) is assumed to be applicable to those ions which are free, is perhaps more sound, theoretically, than the extensions of Gronwall-La Mer and of Müller. In order to avoid these difficulties Guggenheim‡ has allowed for the deviations which must occur from the ideal inter-ionic treatment at appreciable concentrations, by combining the 'specific interaction principle' of Brønsted (p. 127) with the simple Debye-Hückel behaviour. If $f_{R,X}$ is the activity coefficient of the electrolyte RX then

$$\log f_{R,X} = \log f_{\pm}^{\text{stand.}} + \log f_{R,X}^{\text{spec.}} \quad \dots \quad (\text{xli})$$

where $f_{\pm}^{\text{stand.}}$ represents the Debye-Hückel value and $f^{\text{spec.}}$ represents an empirical correction for the specific properties of the ions present in the electrolyte. The latter has so far only been obtained empirically, but the idea has interesting possibilities. It is evident, from what has been stated, that there are still many difficulties in the way of a complete treatment of strong electrolytes, but there is little doubt that the Debye-Hückel theory is, in general, applicable for dilute solutions in media of relatively high dielectric constant, and that it represents an important step in the direction of finding a physical interpretation of what was for several years a purely empirical quantity, namely the activity coefficient of an ion.

Debye-Hückel Theory and Conductivity §—According to

* *loc. cit.*

† *loc. cit.*

‡ *loc. cit.* See also, Bonino *et al.*, *Mem. R. Accad. d'Italia Sci. fis.*, 1933, 4, 415, 445, 465; Brüll, *Gazzetta*, 1934, 64, 607, 624.

§ Debye and Hückel, *Physikal. Z.*, 1923, 24, 305; 1924, 25, 145; *Trans. Faraday Soc.*, 1927, 23, 334; for reviews, see Falkenhagen and Williams (J. W.), *Chem. Reviews*, 1929, 6, 317; Williams (J. W.), *ibid.*, 1931, 8, 303; Hartley (H.) *et al.*, *Ann. Reports Chem. Soc.*, 1930, 27, 326; Falkenhagen, *Rev. Mod. Physics*, 1931, 3, 412; *Electrolytes* (Eng. trans., R. P. Bell), 1934; MacInnes *et al.*, *Chem. Reviews*, 1933, 13, 29; *Trans. Amer. Electrochem. Soc.*, 1934, 66, 237; Eucken-Wolf, *Hand- und Jahrbuch Chemischen Physik*, 1933, Vol. 6, Part II, p. 209 (Ulich). For application of the theory to mixtures, see Bennewitz, Wagner and Küchler, *Physikal. Z.*, 1929, 30, 623; Onsager and Fuoss, *J. Physical Chem.*, 1932, 36, 2689.

the theory every ion in solution is surrounded by an atmosphere in which oppositely charged ions are in excess; as long as the ion is in equilibrium this atmosphere must have central symmetry. When an electric current is passed through the solution so that the ions under consideration move to the right, then each ion during its motion will constantly have to build up its ion atmosphere to the right, whereas the charge density to the left will die out. If this formation and destruction of the charged atmosphere occurred simultaneously then there would be no net force of electrical attraction on the moving ion; in actual conduction, however, it is probable there will be a finite 'time of relaxation' during which the right-hand atmosphere is building up to its equilibrium value whilst the left is decaying. Since the ion atmosphere has a charge opposite in sign to that of the moving ion itself it follows that there will always be an excess of ions of opposite sign to the left of the moving ion, and these will retard its motion. This influence on ionic mobility is frequently known as the 'relaxation' or 'asymmetry' effect, since it arises from the lack of central symmetry in the electrical atmosphere surrounding a moving ion. The effect increases, as might be expected, with increasing concentration, and according to Debye and Hückel it is proportional to $u_i \epsilon^2 z_i^2 \kappa / DkT$, for an ion of the i th kind, where u_i is its velocity, and the other symbols have the same significance as previously.* Another factor which will help to reduce the velocity of an ion is the tendency of the applied *E.M.F.* to move the ionic atmosphere, with its associated solvent molecules, in a direction *opposite* to that in which the ion, accompanied by solvent molecules, is itself moving; hence an additional retarding influence is exerted equivalent to an increased viscous resistance of the solvent. This is called the 'electrophoretic' effect, since it is analogous to that which opposes the movement of a colloidal particle in an electrical field: it is related to the quantity $\epsilon z_i \kappa r$, where r is the radius of the moving ion.† In addition to these two effects the force due to the applied *E.M.F.* is also opposed by the normal frictional resistance of the medium, which may be determined by the aid of Stokes' law.

When the ion moves with a steady velocity the four forces balance one another. By combining the formulæ giving their values Debye and Hückel obtained, for a uni-univalent electrolyte in dilute solution, the expression

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \left[\frac{r_1 \rho_2 + r_2 \rho_1}{\rho_1 + \rho_2} + \frac{\rho_1^2 + \rho_2^2}{2\rho_1 \rho_2} \cdot \frac{\epsilon^2}{6DkT} \right] \kappa \quad (\text{xlvi})$$

where Λ_0 and Λ are the equivalent conductances at infinite dilu-

* It should be noted that κ involves the square-root of the concentration.

† Cf., however, Hermans, *Z. Physik*, 1935, 97, 681.

tion and at a small concentration c respectively, r_1 and r_2 are the radii of the positive and negative ions, and ρ_1 and ρ_2 the frictional coefficients which multiplied by the ionic velocity give the frictional force of the medium overcome during steady movement of the ion. If the ions are assumed to obey Stokes' law, then

$$\rho_1 = 6\pi\eta r_1 \text{ and } \rho_2 = 6\pi\eta r_2$$

$$\text{and } \frac{\Lambda_0 - \Lambda}{\Lambda_0} = \left[\frac{1}{3\pi\eta} \cdot \frac{\rho_1\rho_2}{\rho_1 + \rho_2} + \frac{\rho_1^2 + \rho_2^2}{2\rho_1\rho_2} \cdot \frac{\varepsilon^2}{6DkT} \right] \kappa \quad (\text{xlvi})$$

In order to simplify this expression another aspect of conductance must be considered. The conducting power of a solution is equal to Σncu , where n is the number of ions present, ε the charge carried by each ion, and u the ionic velocity, all in appropriate units. When the ion is moving with a steady velocity in a solution at infinite dilution the frictional force, ρu , is exactly balanced by the electrical force $V\varepsilon$ acting on the ion, where V is the fall of potential through the electrolyte. If V is assumed to be unity, then $u = \varepsilon/\rho$, and the conducting power of the solution is $\Sigma n\varepsilon^2/\rho$. For a solution containing 1 gm. mol. (= 1 gm. equiv. for a uni-univalent compound) of electrolyte per litre, then

$$\Lambda_0 = \frac{N\varepsilon^2}{\rho_1} + \frac{N\varepsilon^2}{\rho_2} = N\varepsilon^2 \left(\frac{\rho_2 + \rho_1}{\rho_1\rho_2} \right) \quad (\text{xli})$$

where N is the Avogadro number, and appropriate units are used for ε and ρ . Hence

$$\frac{\rho_1\rho_2}{\rho_1 + \rho_2} = \frac{N\varepsilon^2}{\Lambda_0} \quad (\text{li})$$

Substituting in equation (xlvi) it is found that

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \left[\frac{1}{3\pi\eta} \cdot \frac{N\varepsilon^2}{\Lambda_0} + \frac{\rho_1^2 + \rho_2^2}{2\rho_1\rho_2} \cdot \frac{\varepsilon^2}{6DkT} \right] \kappa \quad (\text{lii})$$

Introducing the expression for κ (p. 139), and the numerical values of D , k , N , ε , η , π and T for water at 18°, the right-hand side of the equation may be simplified; it follows that

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \left[\frac{49.8}{\Lambda_0} + 0.390 \frac{\rho_1^2 + \rho_2^2}{2\rho_1\rho_2} \right] \sqrt{c} \quad (\text{liia})$$

where c is the concentration of the electrolyte in gm. equiv. per litre. Since the frictional coefficients (ρ) are inversely proportional to the ionic velocities (u) the equation reduces to

$$-\Lambda = \left[49.8 + 0.390\Lambda_0 \frac{u_1^2 + u_2^2}{2u_1u_2} \right] \sqrt{c} \quad (\text{liib})$$

For a dilute solution u_1 and u_2 may be regarded as constant for a given electrolyte, hence

$$\Lambda_0 - \Lambda = k\sqrt{c} \quad (\text{liic})$$

which is identical in form with the empirical equation suggested by Kohlrausch (p. 68). The value of k may be calculated provided the ionic mobilities are known, but the results are not in very good agreement with those observed; thus for potassium chloride the calculated value is 100.6 and the experimental figure is 84.7. Redlich* considered that Stokes' law should be modified in order to apply to particles of molecular dimensions, so as to take the form

$$\rho = \frac{1}{\phi} \cdot 6\pi\eta r$$

where ϕ equals 0.694 for uni-univalent electrolytes. This alters equation (lib) to the extent of replacing 49.8 by 35.0, and so for potassium chloride k is calculated as 86.4.

The Onsager Extension—A further theoretical development has been made by Onsager,† who suggested that the Debye-Hückel calculation of the electrical force due to the asymmetry of the ionic atmosphere must be modified on account of the natural Brownian motion of the ions. The equation deduced for a binary electrolyte was

$$\Lambda_0 - \Lambda = \left[\frac{29.0(z_+ + z_-)}{(DT)^{0.5}\eta} + \frac{0.986 \times 10^6}{(DT)^{1.5}} w \Lambda_0 \right] \sqrt{2\mu} \quad (\text{liii})$$

where
$$w = z_+ z_- \frac{2q}{1 + \sqrt{q}}$$

and
$$q = \frac{z_+ z_- (u_1 + u_2)}{(z_+ + z_-) (z_- u_1 + z_+ u_2)}.$$

For a uni-univalent electrolyte this reduces to the form

$$\Lambda = \Lambda_0 - (A + B\Lambda_0)\sqrt{c} \quad (\text{liv})$$

where A and B are constants dependent on the solvent and the temperature only. The calculated values at 25° for water and methyl and ethyl alcohols are as follows:

	A	B
Water	59.8	0.227
Methyl alcohol	158.1	0.957
Ethyl alcohol	91.9	1.44

For any given electrolyte in a given solvent the variation of equivalent conductance with concentration should thus be represented by the equation

$$\Lambda = \Lambda_0 - k\sqrt{c} \quad (\text{liva})$$

where k is a constant equal to $A + B\Lambda_0$.

* *Physikal. Z.*, 1925, 26, 199.

† *Ibid.*, 1926, 27, 388; 1927, 28, 277; *Trans. Faraday Soc.*, 1927, 23, 341; see also reviews mentioned on p. 157 *supra*.

Tests of the Conductance Equation*—The general form of the Debye-Hückel-Onsager equation requires the equivalent conductance to vary in a linear manner with the square-root of the concentration of the electrolyte. There is little doubt, from the large amount of data accumulated in recent years that, for dilute solutions in solvents of dielectric constant greater than about 20, this relationship holds good.† The presence of the square-root term in the conductance equations is a consequence of the application of Coulomb's law to the inter-ionic actions, and so it may be supposed that this is justifiable, but the real test of the Debye-Hückel-Onsager treatment must lie in a comparison of the values of k in equation (liv), representing the slope of the plot of Λ against \sqrt{c} , determined experimentally and those calculated from the known A and B values. In water and methyl alcohol a number of simple salts, especially alkali halides, give slopes in excellent agreement with those determined from equation (liv), and even where differences exist they are not of large magnitude. Similar results have been obtained for solutions in ethyl alcohol, although in this case the deviations from theoretical behaviour are somewhat larger. In non-hydroxylic solvents, such as nitriles, nitro-compounds and ketones, some salts give plots of Λ against \sqrt{c} with slopes very close to those calculated, but others may be several hundred per cent. different.

The fact that there are as many instances in which the Onsager equation represents almost exactly the variation of conductance with concentration in dilute solution provides very powerful support for the general theory of inter-ionic attraction, based on the supposition of complete dissociation of strong electrolytes. It is necessary, therefore, to inquire into the causes of the deviations from the 'ideal' behaviour, which, in general, fall into two categories. In the first place, certain salts, e.g. sodium and potassium chlorides, give conductances at low concentrations which are in excellent agreement with the calculated amounts, but at appreciable concentrations the measured conductances are somewhat larger than those

* For references see review articles mentioned on p. 157 and those given below; see also pp. 68, 137.

† For summaries, see Davies, *The Conductivity of Solutions*, 1933, Chap. V; Hartley (H.) *et al.*, *Ann. Reports*, 1930, 27, 341; *Chemistry at the Centenary* (1931) *Meeting of the Brit. Assoc.*, p. 25; Philip, *ibid.*, p. 54; Mead, Hughes (O. L.) and Hartley (H.), *J. Chem. Soc.*, 1933, 1207; Barak and Hartley, *Z. physikal. Chem.*, 1933, 165, 272; Walden and Birr, *ibid.*, 1933, 163, 321; Ekwall, *ibid.*, p. 442; Sementschenko and Serpinsky, *ibid.*, 1934, 167, 197; Shedlovsky, Brown (A. S.) and MacInnes, *Trans. Amer. Electrochem. Soc.*, 1934, 66, 237; Jones (G.) and Bickford, *J. Amer. Chem. Soc.*, 1934, 56, 602; Coates and Taylor (E. G.), *J. Chem. Soc.*, 1936, 1245, 1495.

calculated. It is possible, however, to make in the following manner an empirical correction, which probably has its theoretical basis in the approximations, such as neglect of effects due to the size of the ions, of interactions between the various retarding effects affecting ionic velocities, and of the neglect of higher terms in expansions of series, made in the deduction of the Onsager equation.* It is possible to write equation (liv) in the form

$$\Lambda_0 = \frac{\Lambda + A\sqrt{c}}{1 - B\sqrt{c}} \quad \text{. (lv)}$$

and by adding terms involving c and $\log c$, this becomes

$$\Lambda_0 = \frac{\Lambda + A\sqrt{c}}{1 - B\sqrt{c}} - Cc + Dc \log c \quad \text{(lvi)}$$

where C and D are empirical constants.† In some cases D is almost zero and the last term is unnecessary. This equation represents the behaviour of electrolytes in relatively concentrated solutions,‡ but reduces to the simple Onsager form at high dilutions.

Incomplete Dissociation.—The second type of deviation from the Onsager equation has received considerable attention: it is concerned with the fact that many electrolytes give straight-line plots of Λ against \sqrt{c} , but the slopes are numerically greater than the calculated value of k ; this means that the conductances are less than those to be expected from equation (liv). It is generally agreed that this difference is to be accounted for by the fact that not all the ions may be free to conduct the current: some may be held together by chemical forces in the form of un-ionized molecules, as is certainly the cases with many acids and bases, but with most salts some ions will exist as associated ion-pairs (see p. 155) and be unable to conduct current. Some support for this view is obtained from the fact that the deviations under consideration are more marked the smaller the ions, the higher the valency and the lower the dielectric constant of the medium,§ as is to be expected from Bjerrum's treatment of ion association. This idea has been developed as a means of calculating the degree of dissociation of an electrolyte, or in other words, the average fraction of the solute free to carry current,|| the basic assumption being that

* Cf. Onsager and Fuoss, *J. Physical Chem.*, 1932, **36**, 2689; Fuoss, *Physikal. Z.*, 1934, **35**, 59.

† Shedlovský, *J. Amer. Chem. Soc.*, 1932, **54**, 1405, 1411; 1934, **56**, 1066.

‡ See, however, Jones (G.) and Bickford (*loc. cit.*).

§ See, for example, Davies, *op. cit.*, p. 83; Mead, Hughes and Hartley *loc. cit.*

|| It should be emphasized that the method of calculation cannot distinguish between true un-ionized molecules and associated ion-pairs.

the conductance of the free ions is that required by the Onsager equation. In equation (lvia) the quantity Λ represents the conductance of 1 gm. equiv. of electrolyte at concentration c , when *completely* in the form of *free* ions, the term $k\sqrt{c}$ being the diminution from the value at infinite dilution due to inter-ionic forces. If only the fraction α of the 1 gm. equiv. is present as free ions—this is the so-called degree of dissociation—then the concentration of free ions is αc , and the inter-ionic term becomes $k\sqrt{\alpha c}$; the conductance of 1 gm. equiv. of *free* ions at this concentration, which may be called Λ' , is then given by

$$\Lambda' = \Lambda_0 - k\sqrt{\alpha c} \quad \text{. (lvii)*}$$

Actually, however, 1 gm. equiv. of electrolyte only contains α gm. equiv. as free ions, so that the measured equivalent conductance Λ is thus

$$\Lambda = \alpha(\Lambda_0 - k\sqrt{\alpha c}) \quad \text{. (lviii)}$$

and from equations (lvii) and (lviii) it is seen that the true degree of dissociation α is Λ/Λ' , and not Λ/Λ_0 (p. 78). For weak electrolytes, however, Λ' and Λ_0 do not differ very considerably, but for relatively strong electrolytes the difference may be considerable.

Several methods may be used to calculate α and Λ' : Davies † writes equation (lvii) in the form

$$\Lambda' = \Lambda_0 - k\sqrt{\Lambda c/\Lambda'} \quad \text{. (lviaa)}$$

the value of k being obtained from the Onsager equation, that is $A + B\Lambda_0$, an adequate value of Λ_0 being obtained by extrapolation or from the known ion conductances (p. 72). By inserting the measured equivalent conductance Λ at the known concentration c , and using Λ_0 for Λ' under the square-root sign, a first approximation to Λ' is obtained from equation (lviaa); this is then used in the $\sqrt{\Lambda c/\Lambda'}$ term and a more accurate value of Λ' computed. The process is continued until Λ' remains constant: from this α at the given concentration may be determined. It has been shown by Banks ‡ that for most purposes the Onsager equation, allowing for incomplete dissociation, may be written

$$\Lambda' = \{\Lambda_0^2 - 2k\sqrt{(\Lambda_0 \Lambda c)}\}^{0.5} \quad \text{. (lix)}$$

and this may be used to determine Λ' directly from Λ_0 , Λ and c , which are known.

* The quantity called Λ' can be determined from experimental observations in some cases, as shown on p. 79: it is equal to the sum of the ionic mobilities at the particular ionic concentration of the electrolyte.

† *Trans. Faraday Soc.*, 1927, 23, 351; *op. cit.*, p. 101; cf. also *J. Physical Chem.*, 1925, 29, 977; *Phil. Mag.*, 1927, 4, 244.

‡ *J. Chem. Soc.*, 1931, 3341; for application, see Dippy and Williams (F. R.), *ibid.*, 1934, 161.

Dissociation Constants—The degree of dissociation determined in the manner described may be combined with the activity aspect of the Debye-Hückel concepts to calculate true, or thermodynamic, dissociation constants, especially for weak or moderately strong electrolytes. It has been already seen that the law of mass action should be applicable even if the so-called undissociated molecules are actually ion-pairs, and so for a binary electrolyte BA it follows (see equation xlv, p. 115) that

$$K = \frac{[B'] [A'] f_B f_{A'}}{[BA] f_{BA}}$$

If c is the stoichiometrical concentration of the electrolyte and α the degree of dissociation, determined as described above, then the concentration of each of the ions will be αc , and that of undissociated molecules $(1 - \alpha)c$; assuming the activity coefficient (f_{AB}) of the latter to be unity, the above equation becomes

$$K = \frac{\alpha^2 c}{1 - \alpha} f_B f_{A'} \quad \text{(lx)}$$

In the simple Debye-Hückel equation for the activity coefficient of a univalent ion, viz. $\log f = -A\sqrt{\mu}$, the ionic strength (μ) is readily shown to be equal to αc , and substituting in equation (lx) it is seen that

$$\log \alpha^2 c / (1 - \alpha) = \log K + 2A\sqrt{\alpha c} \quad \text{(lxi)}$$

This equation is particularly applicable to relatively weak electrolytes in which the ionic concentration is so low that the limiting form of the Debye-Hückel equation can be used. It can be tested by plotting $\log \alpha^2 c / (1 - \alpha)$ against $\sqrt{\alpha c}$ for solutions of different concentrations, when a straight line should be obtained: the extrapolated intercept for infinite dilution ($c = 0$) gives $\log K$, and the slope should correspond with the value of A required by the Debye-Hückel equation, e.g. 0.505 for water at 25°. Alternatively K may be evaluated from equation (lxi) for each of a series of solutions, and if the equation is satisfactory the results should be constant over an appreciable range of concentration. In one or other of these ways equation (lxi) has been verified from conductivity data on weak and moderately strong acids* as well as on bi-bivalent salts, e.g. sulphates and oxalates, which appear to be undissociated to an appreciable extent. With uni-bivalent salts a modified relationship involving an extended form of the Debye-Hückel theory,

* Davies, *op. cit.*, Chap. VII; *J. Amer. Chem. Soc.*, 1932, **54**, 1698; MacInnes and Shedlovsky, *ibid.*, p. 1429; 1935, **57**, 1705; Saxton *et al.*, *ibid.*, 1933, **55**, 3638; 1934, **56**, 1918; Brockman (F. G.) and Kilpatrick (M.), *ibid.*, p. 1483; Murray-Rust and Hartley (H.), *Proc. Roy. Soc.*, 1929, **126 A**, 84.

namely equation (xxxa), has been employed with satisfactory results. In other cases, e.g. uni-univalent salts, constant values of K have been obtained by the use of experimental activity data.* On the whole the calculations can be said to lend strong support to the theory of inter-ionic action, provided incomplete dissociation, which may be chemical or physical in nature, is taken into account. It has already been recorded (p. 129) that allowance for incomplete dissociation makes the rule that the activity coefficient is a function only of the ionic strength valid at higher concentrations than otherwise: this rule is, of course, implied in the simple Debye-Hückel equation.

An alternative method of combining the results of the theory of inter-ionic attraction for weak and intermediate electrolytes, has been worked out by Fuoss,† a somewhat more tedious solution of the same equations having been used previously by Fuoss and Kraus.‡ A variable x is defined by the expression

$$x = k\sqrt{c\Lambda}/\Lambda_0^{1.5} \quad \text{. (Ixii)}$$

where k is the Onsager constant, and then the equation (Iviii) may be written in the form

$$\Lambda = \alpha\Lambda_0 F(x) \quad \text{. (Ixiii)}$$

where $F(x)$ is a function of x , thus

$$F(x) = \frac{4}{3} \cos^2 \frac{1}{3} \cos^{-1}(-\frac{3}{2}x\sqrt{2}) \quad \text{. (Ixiv)}$$

Values of this function, from $x = 0$ to 0.209, have been worked out and tabulated, so as to simplify the application of the method. Turning to equation (Ix) it follows that since the Debye-Hückel theory requires both ions in a dilute solution of AB to have the same activity coefficient, this may be written

$$K = \alpha^2 cf^2 / (1 - \alpha) \quad \text{. (Ixv)}$$

where f represents the activity coefficient of either ion, or the mean value for the electrolyte. Inserting Λ/Λ' for α , where Λ' is given by equation (Ivii), it is seen that

$$K = \Lambda^2 cf^2 / \Lambda'(\Lambda' - \Lambda) \quad \text{. (Ixvi)}$$

$$\text{and } \Lambda cf^2 / K\Lambda_0^2 = \Lambda'(\Lambda' - \Lambda) / \Lambda\Lambda_0^2 \quad \text{. (Ixvii)}$$

From equation (Ixiii) it follows that $\Lambda' = \Lambda_0 F(x)$, and substituting this for Λ' in equation (Ixvi) there is obtained

$$\frac{\Lambda cf^2}{F(x) K\Lambda_0^2} + \frac{1}{\Lambda_0} = \frac{F(x)}{\Lambda} \quad \text{. (Ixviii)}$$

* Davies *et al.*, *Trans. Faraday Soc.*, 1927, 23, 351; 1930, 26, 592; 1931, 27, 621; 1932, 28, 609; see also, Martin, *J. Chem. Soc.*, 1928, 3270; 1930, 530.

† *J. Amer. Chem. Soc.*, 1935, 57, 488; see also, *Trans. Faraday Soc.*, 1936, 32, 594.

‡ *J. Amer. Chem. Soc.*, 1933, 55, 476; see also, Shedlovsky and Uhlig, *J. Gen. Physiol.*, 1934, 17, 549.

This relationship means that if $\Lambda c f^2/F(x)$ is plotted against $F(x)/\Lambda$ a straight line should be obtained, the slope giving $1/K\Lambda_0^2$ and the intercept for infinite dilution gives $1/\Lambda_0$; hence both Λ_0 and K can be determined. In applying equation (lxviii) the activity coefficients are derived from the simple Debye-Hückel equation, and $F(x)$ is taken for an x value given by equation (lxii), using an approximate estimate of Λ_0 obtained by extrapolation of Λ against \sqrt{c} . It appears that the final results are not greatly affected by this approximation, although the process could be repeated if necessary after a first value of Λ_0 has been obtained.* The experimental data of Fuoss and Kraus and their collaborators,† of conductivities in media of low dielectric constant, provide strong arguments for the inter-ionic attraction theory: as already mentioned (p. 156) their values for the dissociation constant are in harmony with Bjerrum's concept of ion-pairs.

Transport Numbers and Onsager's Equation—For a particular univalent ion the Onsager equation may be written

$$\Lambda_i = (\Lambda_i)_0 - k_i \sqrt{c} \quad \text{. (lxix)}$$

and since the transport number of the cation can be represented by

$$n_c = \Lambda_c / (\Lambda_c + \Lambda_a) \quad \text{. (lxx)}$$

where the suffixes c and a indicate cation and anion, respectively, it can be readily shown that the transport number is, in general, given by an equation of the type

$$n = \frac{A}{1 + B\sqrt{c}} C \quad \text{. (lxxi)}$$

where A , B and C are constants dependent on the nature of the electrolyte.‡ This should represent the variation of transport number with concentration in dilute solutions. It may be noted that this equation is identical in form with an empirical one proposed by Jones and Dole (p. 39) although, as already indicated, the values of the constants do not agree. By dividing through with the denominator, equation (lxxi) takes the series form

$$n = (A - C) - AB\sqrt{c} + AB^2c - \text{. (lxxia)}$$

and when c is small this becomes the same as the Scatchard equation (p. 39).

* For alternative solutions of the same fundamental Debye-Hückel and Onsager equations, involving successive approximations, see Davies, *J. Chem. Soc.*, 1933, 645; Ives, *ibid.*, p. 731; they were proposed as methods for determining Λ_0 , and are applicable, like that described above, for weak and intermediate electrolytes; for strong electrolytes the method of Onsager (*Physikal. Z.*, 1927, 28, 277) may be employed.

† For references, see p. 156.

‡ Dole, *J. Physical Chem.*, 1931, 35, 3647.

By introducing the transport number at infinite dilution (n_0) as defined by the appropriate form of equation (lxx) it can be deduced that

$$n = n_0 + \left(\frac{2n_0 - 1}{\Lambda'} \right) B\sqrt{c} \quad \dots \quad (\text{lxxii})$$

where Λ' is a quantity involving Λ_0 , k and c , which becomes equal to Λ_0 at infinite dilution, that is when $c = 0$, and B is equal to $A/2$ of the Onsager equation (liv). Differentiating equation (lxx) with respect to \sqrt{c} , it is seen that if the transport number is plotted against the square-root of the concentration, the slope of the curve as infinite dilution is approached should become equal to $(2n_0 - 1)B/\Lambda_0$: this expectation is in general agreement with the experimental results.*

Conductance with High Frequency and High Voltage Currents †—If a high frequency alternating voltage is applied to an electrolyte and the time of oscillation of an ion is equal to, or less than, the 'relaxation time', the unsymmetrical charge distribution, generally produced around an ion in motion, can no longer form completely; the retardation of the ionic velocity resulting from the asymmetry of the ion atmosphere thus disappears partially or completely, and the conductance of the solution is greater than the normal value obtained with low frequency alternating or with direct current. The electrophoretic effect, however, will not be affected by the high frequency oscillations, since the ionic atmosphere, although symmetrical, still remains. The time of relaxation has been calculated as of the order $10^{-10}/c$ sec., where c is the concentration of the electrolyte; for a 0.001*N* solution, the time is about 10^{-7} sec., and the effect on the conductance of high frequency oscillations with a wavelength of 1 metre (oscillation time 3.3×10^{-8} sec. approx.) should be noticeable. The increase of conductance at high frequencies was deduced theoretically by Debye and Falkenhagen,‡ and subsequently verified by Sack § and

* Longworth, *J. Amer. Chem. Soc.*, 1932, **54**, 2741; 1935, **57**, 1185; Owen, *ibid.*, p. 244; see also Onsager and Fuoss, *J. Physical Chem.*, 1932, **36**, 2689.

† It is of interest to record that the effects of high frequency and high voltage currents on conductance were predicted by Sand (*Phil. Mag.*, 1923, **45**, 281) on the assumption of complete ionization of strong electrolytes, before the Debye-Hückel theory was published.

‡ Debye and Falkenhagen, *Physikal. Z.*, 1928, **29**, 121, 401; *Z. Elektrochem.*, 1928, **34**, 562; Falkenhagen and Williams (J. W.), *Z. physikal. Chem.*, 1928, **135**, 399; *J. Physical Chem.*, 1929, **33**, 1121; see also, Debye, *Z. Elektrochem.*, 1933, **39**, 478; Falkenhagen and Fischer (W.), *ibid.*, p. 517; *Physikal. Z.*, 1932, **33**, 941; 1933, **34**, 593, 786; Wien, *Ann. Physik*, 1931, **11**, 429; *Physikal. Z.*, 1933, **34**, 625.

§ *Ibid.*, 1928, **29**, 627.

others.* The *fractional* diminution of the asymmetry effect (p. 158) for oscillations of a given frequency is, in general, greater the lower the valency of the ions and their concentration, and the higher the dielectric constant and the temperature; the results are in approximate quantitative agreement with the theoretical anticipations.

An increase in the conductance of an electrolyte was observed by Wien† when using very high applied voltages, of the order of 20,000 volts per cm.; in these circumstances an ion moves at a speed of about 1 metre per second (instead of a normal value of about 0.01 mm. per sec.), and so travels many times the thickness of its ionic atmosphere during the time of relaxation. As a result the moving ion is virtually free from an oppositely charged atmosphere, and so neither asymmetry nor electrophoretic effects are operative and the conductance should approach the value at infinite dilution. With increasing voltage, therefore, Ohm's Law apparently breaks down for electrolytes. The theory of the influence of high voltages on conductance has been worked out,‡ and the experimental results appear to be in general harmony.§ The relative increase of equivalent conductance increases with decreasing concentration and increasing valency of the ions. It was thought at one time that since the effect of inter-ionic attraction on conduction is eliminated by the use of high voltages, a method would be available for determining the true degree of dissociation of an electrolyte from conductance measurements. If $\Lambda^{\text{H.V.}}$ is the limiting value for the equivalent conductance at high voltages, then the degree of dissociation should be $\Lambda^{\text{H.V.}}/\Lambda_0$. It has been found, however, that with weak acids and bases, which are known to be ionized to a relatively small extent, the effect of high voltages on the conductance is much greater

* Zahn, *Z. Physik*, 1928, 51, 350; Rieckhoff, *Ann. Physik*, 1929, 2, 577; Rieckhoff and Zahn, *Z. Physik*, 1929, 53, 619; Brendel *et al.*, *Physikal. Z.*, 1929, 30, 576; 1930, 31, 345; 1931, 32, 327; Mizushima and Sack, *ibid.*, 1930, 31, 811; Deubner, *Ann. Physik*, 1930, 5, 305; *Physikal. Z.*, 1932, 33, 223; Gaertner, *ibid.*, 1931, 32, 919; Spaght, *ibid.*, 1932, 33, 534; Schaefer, *Z. Physik*, 1932, 77, 117; Wenk, *Ann. Physik*, 1933, 17, 679; Glowatski, *ibid.*, 1933, 18, 660; Whitmore, *Physikal. Z.*, 1933, 34, 649; Geest, *ibid.*, p. 660; Debye and Sack, *Z. Elektrochem.*, 1933, 39, 512; Harada, *Bull. Inst. Phys. Chem. Res. Japan*, 1934, 13, 1340; Hiegemann, *Ann. Physik*, 1936, 25, 337.

† *Ibid.*, 1927, 83, 327; 1928, 85, 795; *Physikal. Z.*, 1927, 28, 834.

‡ Joos and Blumentritt, *ibid.*, p. 836; 1928, 29, 755; Blumentritt, *Ann. Physik*, 1928, 85, 812; 1929, 1, 915; Falkenhagen, *Physikal. Z.*, 1931, 32, 353; Wien, *ibid.*, p. 545; Debye, *Z. Elektrochem.*, 1933, 39, 478.

§ Wien, *loc. cit.*, 1927 and 1928; Bauer, *Ann. Physik*, 1930, 6, 253; Possner, *ibid.*, p. 875; Schiele, *Ann. Physik*, 1932, 7, 811; Fuchs, *ibid.*, 1932, 12, 306; Hüter, *ibid.*, 1935, 24, 253; see also Malsch and Hartley (G. S.), *Z. physikal. Chem.*, 1934, 170, 321.

than is to be expected.* There is reason to believe that the powerful electrical fields have, in these instances, a tendency to split up the undissociated molecules into ions;† if this is the case then the method proposed for determining the degree of dissociation would be unreliable.

Viscosity—It was observed by Jones (G.) and Dole that the viscosity of an electrolyte could be represented by an equation of the type

$$\eta/\eta_0 = 1 + A\sqrt{c} + Bc \quad \dots \quad (\text{lxiii})$$

where η and η_0 are the viscosities of solution and solvent, respectively, A and B are constants, and c is the concentration: this result, since it included the square-root of the concentration, was in agreement with the authors' anticipation that the viscosity of an electrolyte was related to the inter-ionic forces.‡ Following this suggestion Falkenhagen and Dole§ showed that an equation for the relative viscosity, containing the first two terms of equation (lxiii) could be deduced theoretically for a simple electrolyte having two ions with the same velocity; later the treatment was extended to the general case for ions of any valency or mobility.|| The argument used is based on the view that during the flow of an electrolyte the oppositely charged atmosphere of any ion will be deformed, with the result that a shearing force is set up which tends to oppose the flow and hence increase the viscosity. The magnitude of this force is determined by the Coulomb attraction between the ion and its atmosphere. In this manner the square-root term in equation (lxiii) can be accounted for and theoretical values of A calculated; the mathematical treatment for dilute solutions, however, does not include the B term. Experimental studies of the viscosity of electrolytes have confirmed the satisfactory nature of the equation of Jones and Dole, and the observed values of A are in excellent agreement with those calculated: the results are definitely to be regarded as evidence for the inter-ionic attraction theory.** This work on the viscosity

* Schiele, *Ann. Physik*, 1932, 7, 811; *Physikal. Z.*, 1933, 34, 60; see also Gyemant, *ibid.*, 1927, 28, 834.

† Onsager, *J. Chem. Physics*, 1934, 2, 599.

‡ *J. Amer. Chem. Soc.*, 1929, 51, 2950; see also, Sutherland, *Phil. Mag.*, 1907, 14, 1.

§ *Z. physikal. Chem.*, 1929, B, 6, 159; *Physikal. Z.*, 1929, 30, 611.

|| Falkenhagen, *ibid.*, 1931, 32, 365; Falkenhagen and Vernon, *ibid.*, 1932, 33, 140; *Phil. Mag.*, 1932, 14, 537; see also Onsager and Fuoss, *J. Physical Chem.*, 1932, 36, 2689.

** Wolfenden *et al.*, *Proc. Roy. Soc.*, 1931, 134 A, 413; 1934, 145 A, 475; *J. Chem. Soc.*, 1931, 403; 1934, 1144; Jones (G.) *et al.*, *J. Amer. Chem. Soc.*, 1933, 55, 624, 4124; 1935, 57, 2041; 1936, 58, 619; Hood and Hohlfelder, *J. Physical Chem.*, 1934, 38, 978; Glass and Madgin, *J. Chem. Soc.*, 1934, 1124; Tollert, *Z. physikal. Chem.*, 1935, 172, 129.

of strong electrolytes has raised the question of whether the viscosity should be included in determining the degree of dissociation of an electrolyte (see p. 78), since the asymmetry factor involved in the Debye-Hückel-Onsager treatment is really the same as that responsible for the increased viscosity. The use of the methods for determining α described on pages 163 and 165, therefore, appears to avoid the need for a viscosity correction.*

Other Properties—A number of other properties of electrolytes have been shown to depend on the existence of the ionic atmosphere: amongst these may be mentioned the dielectric constant and surface tension. The dispersion of the dielectric constant of an electrolytic solution at high frequencies has been treated theoretically † in a manner analogous to that applied to the effect on conductivity, but definite experimental data do not appear to be available. At constant frequency the theory requires the dielectric constant of a dilute solution to be a linear function of the square root of the concentration, and this has been confirmed by actual measurements.‡ The concept of inter-ionic attraction is also in general agreement with the influence of electrolytes on surface tension.§

Triple Ions—Although not directly related to the ionic atmosphere treatment of the conductance of electrolytes, the concept of triple ions has an important bearing on the subject of inter-ionic attraction. Extending the ion-association idea of Bjerrum, it has been suggested by Fuoss and Kraus || that groups of three ions, viz. $+ - +$ or $- + -$, might form associated triplets, especially in solvents of low dielectric constant. According to Fuoss ** this should be expected to commence *in such media* at a concentration of about $3.2 \times 10^{-7} D^3$ gm. ions per litre, for a uni-univalent salt at 25° , and the formation of ion clusters would account for the failure of the Onsager equation in these solvents. Consider an electrolyte AB in a solvent of low dielectric constant: even if it is completely ionized there will be a very large proportion of ion-pairs, and the

* For a discussion, see Jones (G.) and Dole, *J. Amer. Chem. Soc.*, 1930, 52, 2254; cf., however, Davies, *ibid.*, 1932, 54, 3776.

† Debye and Falkenhagen, *Physikal. Z.*, 1928, 29, 121, 401; Falkenhagen *et al.*, 1932, 33, 218, 941.

‡ Fischer (E.), *ibid.*, 1935, 36, 585; Jezewski, *ibid.*, 1936, 37, 52; Fischer (G.) and Schaffeld, *Ann. Physik*, 1936, 25, 450.

§ Wagner, *Physikal. Z.*, 1924, 25, 474; Onsager and Samaras, *J. Chem. Physics*, 1934, 2, 528; Jones (G.) and Ray, *J. Amer. Chem. Soc.*, 1935, 57, 957.

|| *Ibid.*, 1933, 55, 2387.

** *Ibid.*, 1935, 57, 2604; *Chem. Reviews*, 1935, 17, 27. It appears an experimental fact that the Onsager equation breaks down at this concentration in media of low dielectric constant.

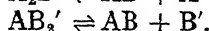
degree of dissociation (α_1) will be small. The dissociation constant (k_1) for the ion-pair equilibrium



is equal to $\alpha_1^2 c / (1 - \alpha_1)$, neglecting activity coefficients, and since α_1 is small, $1 - \alpha_1$ is almost the same as unity; hence k_1 is approximately equal to $\alpha_1^2 c$. If in addition to ion-pairs there are triple ions present, then the following equilibria also exist.



and



The respective mass action constants are given by

$$k_2 = [AB][A']/[A_2B'] \text{ and } k_3 = [AB][B']/[AB_2'] \quad (\text{lxxiv})$$

If the formation of the triple ions is due to electrical effects only, then the existence of A_2B' and of AB_2' is equally probable, and so k_2 and k_3 will be equal; dividing the expression for one by that for the other, it follows that

$$[AB_2']/[A_2B'] = [B']/[A'] \quad (\text{lxxv})$$

The triple ions should thus be formed in the same ratio as that in which the simple ions are present in the solution. If α_3 is the fraction of the total electrolyte present as one of the triple ions, e.g. AB_2' , then $[AB_2']$ is equal to $\alpha_3 c$; since the amount of these ions will be small, $[AB]$ may be taken as approximately equal to the total concentration (c), and $[B']$ can be assumed to remain as $\alpha_1 c$. Substituting in the expression for k_3 , it follows that

$$k_3 = \alpha_1 c / \alpha_3 \quad (\text{lxxvi})$$

and writing k_1 for $\alpha_1^2 c$, as obtained above, it follows that

$$\alpha_3 = \sqrt{k_1 c} / k_3 \quad (\text{lxxvii})$$

If Λ_0 is the sum of the ion conductances of the simple ions at infinite dilution, and λ_0 is the sum for the two kinds of triple ions—since they have a net charge they will carry current—which are formed in the same ratio as the simple ions present (equation lxxv), then, neglecting inter-ionic effects, the observed equivalent conductance (Λ) is

$$\Lambda = \alpha_1 \Lambda_0 + \alpha_3 \lambda_0 \quad (\text{lxxviii})$$

Substituting for α_3 from equation (lxxvii) and noting that $\alpha_1^2 c$ is equal to k_1 , it follows that

$$\Lambda = \Lambda_0 \sqrt{k_1} / \sqrt{c} + (\lambda_0 \sqrt{k_1} / k_3) \sqrt{c} \quad (\text{lxxix})$$

and this is of the form

$$\Lambda = A / \sqrt{c} + B \sqrt{c} \quad (\text{lxxx})$$

where A and B are constants for the given electrolyte. Differentia-

ting this equation with respect to c , the condition for a minimum of equivalent conductance is

$$A = Bc_{\min}. \quad (lxxxix)$$

and it follows that

$$k_3 = (\lambda_0/\Lambda_0)c_{\min}. \quad (lxxxii)$$

and

$$\Lambda_{\min.} = 2(\alpha_1\Lambda_0)_{\min.} = 2(\alpha_3\lambda_0)_{\min.} \quad (lxxxiii)$$

The concept of triple ions thus accounts for the conductance minima which have been frequently observed (see p. 83.) From equation (lxxxii) it is seen that the concentration for the minimum conductance is proportional to k_3 , and so is inversely proportional to the stability of the triple ions. The minimum occurs when the conductance due to the latter is equal to that due to the simple ions; this follows from equation (lxxxiii). Using the Bjerrum treatment, as applied to the stability of ion-pairs, it can be shown that k_3 is approximately proportional to D^3 in the vicinity of the conductance minimum; * hence

$$D^3/c_{\min.} \approx \text{constant} \quad (lxxxiv)$$

and a theoretical basis is given to Walden's rule (p. 84) concerning the relationship between dielectric constant and the concentration at which the equivalent conductance is a minimum. The various consequences of the view that triple ions exist in media of low dielectric constant have been verified by a large number of conductance measurements,† and evidence for the existence of still larger ion clusters has been obtained.‡ The results appear to provide ample justification for calculation of the equilibrium constant for the triple ion equilibrium by the method of Bjerrum, which is based on the supposition that electrostatic forces are responsible for the ion complexes.§

Review of Electrolytic Dissociation and of Solvent Effects

—In reviewing the problems of electrolytic dissociation it is at once evident that as far as the free ions are concerned the views of Debye, Hückel and Onsager give an adequate, although over-simplified, picture of the operation of inter-ionic forces as the cause of the departure of electrolytes from the behaviour of perfect solutions. It should be emphasized, to avoid misunderstanding, that although the Debye-Hückel theory was put forward to explain the behaviour of strong electrolytes, the arguments concerning the ionic atmos-

* For a criticism, see Gross (P.) and Halpern, *J. Chem. Physics*, 1934, 2, 188; and reply by Fuoss and Kraus, *ibid.*, p. 386.

† See references to Fuoss and Kraus, p. 156 (*supra*); also *J. Amer. Chem. Soc.*, 1934, 56, 1857, 1860.

‡ Fuoss and Kraus, *ibid.*, 1933, 55, 3614; Kraus *et al.*, *ibid.*, 1934, 56, 511, 2017, 2265; 1935, 57, 1; *Trans. Faraday Soc.*, 1936, 32, 585.

§ The ion clusters of Fuoss and Kraus must not be confused with true complex ions (see p. 133) which involve covalent linkages.

phere and inter-ionic attractions are applicable to all ions, whether present in strong, intermediate or weak electrolytes. In the latter, however, the deviations from ideal behaviour are relatively small, since the ionic concentration is low. In all electrolytes, except perhaps for very dilute solutions of certain uni-univalent salts, e.g. potassium and sodium chlorides, undissociated molecules are present: it is uncertain, however, whether these are merely ion-pairs held together by electrostatic (Coulomb) forces, in which case the electrolyte may be said to be completely ionized but incompletely dissociated, or whether there are actually present some un-ionized molecules in which the radicals are held together by covalent linkages. As already stated, the law of mass action should be applicable in either case, and so the fact that a definite dissociation constant is obtainable does not help in solving the problem.

It is important to note that Fuoss and Kraus (p. 156) were able to correlate the dissociation constants of quaternary ammonium salts with the dielectric constant of the solvent and the ionic diameters, in the manner required by Bjerrum's treatment based on the existence of electrostatically bound ion-pairs. Further, the results in media of low dielectric constant are in agreement with the concept of triple ions held together by Coulomb forces. It appears, therefore, that the tetra-alkyl-ammonium salts are almost, if not completely, ionized even in low dielectric constant solvents, but that a very large proportion of the ions are held together in groups of two, three or more. It may be recorded also that dilute solutions of these salts, as a general rule, give the ideal Onsager slope for the plot of equivalent conductance against the square root of the concentration, for such solvents as water, nitromethane and acetonitrile.* The deviations in methyl and ethyl alcohols are, however, appreciable and may well be due to ionic association in the media of lower dielectric constant. The extent of the departure from ideal behaviour varies with the nature of both cation and anion, and may be related to their effective size in the solution.† In the molten state the quaternary ammonium salts also appear to be completely ionized.‡

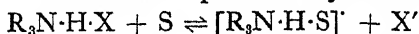
With ammonium salts of the type $R_3NH \cdot X$, however, the general behaviour is quite different: although they are strong electrolytes in hydroxylic solvents, e.g. water and alcohols, they are only dissociated to a small extent in such media as nitrobenzene, nitro-

* Wright, Murray-Rust and Hartley (H.), *J. Chem. Soc.*, 1931, 199; Walden and Birr, *Z. physikal. Chem.*, 1929, 144, 269; 1933, 163, 263, 281.

† See, for example, Mead, Hughes (O. L.) and Hartley (H.), *J. Chem. Soc.*, 1933, 1207.

‡ Walden, *Z. physikal. Chem.*, 1931, 157, 389.

methane, acetone and acetonitrile.* It is unlikely that this difference in behaviour is due to electrostatic forces, since there is little difference in the dielectric constants of the alcohols and of the nitro-compounds: the values in the latter are, in fact, somewhat larger. A much more probable explanation is that the hydrogen atom can act as a link between the nitrogen atom and the acid radical X, so that truly un-ionized molecules are able to exist in solution. The contrast in behaviour between the two groups of solvents is to be explained by their own relative tendencies to co-ordinate with the hydrogen atom. The ionization process may then be represented as



where S is the solvent molecule. If the solvent is an alcohol or water, the oxygen atom can co-ordinate with the hydrogen and ionization takes place to a great extent and the solution behaves as a strong electrolyte. Such solvents as nitro-compounds, nitriles and ketones do not co-ordinate so readily and hence *un-ionized* molecules of $R_3NH \cdot X$ will be present in the solution; these will no doubt ionize to some extent into R_3NH^+ and X^- ions, but the amounts must be small.† In the molten state salts of this type also behave as weak electrolytes, thus indicating the existence of covalent molecules; ‡ the difference in behaviour of the salts $R_3NH \cdot X$ and $R_4N \cdot X$ can hardly be due to the difference in the sizes of the ions, and is presumably to be accounted for by incomplete ionization of the former.

Trimethyl-tin chloride and triphenylmethyl chloride are both non-conductors in the molten state,§ but the former is a relatively good conductor in water and alcohol, || whereas compounds analogous to the latter conduct the electric current when dissolved in liquid sulphur dioxide.** Neither of the chlorides forms a conducting solution in nitrobenzene. Since both tin and carbon are normally four-covalent in these compounds, it is clear that they must be able to exist in un-ionized forms: in suitable solvents there is partial splitting up into ions. These facts and those recorded above not only suggest that salts may be partly un-ionized, but they also emphasize the rôle of the solvent. Although it has been shown that certain salts may exist as un-ionized molecules, the same factors favouring the formation of covalent linkages are not available in the salts of metallic bases. It is generally accepted that in such salts

* Wynne-Jones, *J. Chem. Soc.*, 1931, 795; Walden and Birr, *loc. cit.*

† Wynne-Jones, *loc. cit.*

‡ Walden, *loc. cit.*

§ See Kraus, *Electrically Conducting Systems*, 1922, p. 321; *J. Amer. Chem. Soc.*, 1924, 46, 2196.

|| Kraus, *op. cit.*, p. 321; Kraus and Callis, *J. Amer. Chem. Soc.*, 1923, 45, 2624.

** Ziegler and Wollschitt, *Annalen*, 1930, 479, 108.

the radicals are held together by electrovalency, so that they should be completely ionized. The distinction between covalency and electrovalency may not, however, be simple: according to the theories based on wave mechanics the wave function of a valency bond may, in general, contain both ionic and non-ionic terms. In salts of the alkali halide type, where both ions have the inert-gas structure, it may be supposed that the ionic terms preponderate, so that covalent molecules have practically no existence. According to Fajans' theory,* however, an electrovalency will tend to pass over into a covalency when the cation is small and the anion large: this is probably another way of saying that these factors favour the non-ionic terms in the wave function of the molecule. Lithium iodide, for example, is soluble in a number of organic liquids, and it is not at all improbable that it can exist as un-ionized molecules in such solutions. If this is the case it is possible that incomplete ionization may occur, although only to a very small extent, with other alkali halides. Refractometric and light-absorption data favour the view that even alkali halide solutions contain a small proportion of un-ionized molecules; † the amount is, however, not more than 5 per cent. in solutions up to a concentration of about 5*N*. With copper, zinc, cadmium, mercury and other salts containing ions which do not have the inert-gas structure, the possibility of non-ionic linkage is increased. ‡ According to the calculations of Davies, § magnesium sulphate is about 50 per cent. dissociated in a 0.1 *M*-solution: it is improbable that the formation of ion-pairs can account for the whole of the remainder. The results with the heavy metal sulphates are similar. In these cases, as with the salts of organic acids, e.g. oxalates and malonates, || the relative co-ordinating tendencies of the anion and of the solvent are of importance in determining the degree of ionization. ** The formation of complexes, such as occur with the halides of copper, zinc, cadmium, mercury and lead, †† and

* Fajans, *Naturwiss.*, 1923, **11**, 165; *Z. Physik*, 1924, **23**, 1; *Z. Krystall.*, 1925, **61**, 18; also *infra*.

† *Idem.*, *Trans. Faraday Soc.*, 1927, **23**, 357 (for review); *Z. physikal. Chem.*, 1928, **137**, 361; *Z. Elektrochem.*, 1928, **34**, 1, 502; von Halban, *ibid.*, p. 489; see also Lange, *Physikal. Z.*, 1928, **29**, 760.

‡ For discussion, see Orr and Butler, *Phil. Mag.*, 1934, **18**, 778.

§ *op. cit.*, p. 110; *Trans. Faraday Soc.*, 1927, **23**, 351.

|| Money and Davies, *Trans. Faraday Soc.*, 1932, **28**, 609; *J. Chem. Soc.*, 1934, 400; Riley *et al.*, *ibid.*, 1929, 2006; 1930, 1642; 1931, 1998; 1932, 514, 1776; 1934, 1440; 1936, 1121; Ives, *ibid.*, 1933, 1360.

** Riley *et al.*, *loc. cit.*; Ives, *loc. cit.*

†† See Fromherz *et al.*, *Z. physikal. Chem.*, 1931, **153**, 321; 1933, 167, 103; *Z. Elektrochem.*, 1931, **37**, 553; Riley, *J. Chem. Soc.*, 1934, 1448; see also, Donnan and Bassett (H. L.), *ibid.*, 1902, 81, 939; Abegg and Labendzinski, *Z. Elektrochem.*, 1904, **10**, 77; Denham *et al.*, *Z. physikal. Chem.*, 1909, **65**, 641; *J. Chem. Soc.*, 1919, **115**, 1269; *J. Amer. Chem. Soc.*, 1923, **45**, 1353; Howell, *J. Chem. Soc.*, 1927, 158.

with the sulphates of other metals,* suggests that un-ionized molecules are present in solution. The complex ions definitely involve covalent linkages and are not ion clusters, for if so the tendency to form AB_2 would be as great as for A_2B (see p. 171).

Further evidence for the existence of un-ionized molecules of certain salts is to be found in a consideration of the compounds of mercury; thus mercuric perchlorate is considerably ionized in aqueous solution, whereas the nitrate, chloride and cyanide make poor conductors in which the salts are probably only slightly ionized.† It has been argued that since silver perchlorate may be extracted completely from benzene solution by means of water, no molecular species is common to both solutions; since the salt is a non-conductor and un-ionized in benzene solution, it appears to be completely ionized in aqueous solution.‡ This argument does not take into account, however, the possibility of the perchlorate existing as solvated molecules in either solution. Further, the fact that it is probably un-ionized in benzene solution shows that such molecules can exist and may be present to a small extent even in water. In the discussion here an attempt has been made to consider some of the main features concerning the relationship between ionization and dissociation, but there are many other aspects of the subject requiring consideration in individual cases.§

Influence of Solvent—It is generally agreed that solvents may be divided into two categories, according to their effect on the dissociation of *salts of all types* dissolved in them. There are firstly the so-called 'levelling' solvents, generally hydroxylic substances, in which different salts show relatively little difference in behaviour, as far as deviations from the Onsager equation are concerned, and secondly there are the 'differentiating' solvents in which individual properties become evident and marked deviations from the ideal inter-ionic behaviour occur.|| It has been suggested** that the difference between the two groups of solvents lies in the fact that the

* McBain and van Rysselberghe, *J. Amer. Chem. Soc.*, 1928, 50, 3009; 1930, 52, 2336; see also, Fried and Casper, *ibid.*, p. 2632.

† Lowry (T. M.) *Trans. Faraday Soc.*, 1928, 24, 1; other examples of similar type will be found in this paper.

‡ Hill (A. E.), *J. Amer. Chem. Soc.*, 1921, 43, 254.

§ For further discussions, see Jacobs and King, *J. Physical Chem.*, 1930, 34, 1013, 1303; 1931, 35, 480, 1922; Davies, *op. cit.*, Chap. XVIII; Ives, *loc. cit.*; Fredenhagen, *Z. physikal. Chem.*, 1931, 152, 321; Ulich, *Z. Elektrochem.*, 1933, 39, 483. For evidence based on Raman spectra, see review article by Hibben (*Chem. Reviews*, 1933, 13, 345).

|| Hartley (H.) *et al.*, *Ann. Reports*, 1930, 27, 342; *Chemistry at the Centenary* (1931) *Meeting of the Brit. Assoc.*, p. 25.

** Wright, Murray-Rust and Hartley (H.), *loc. cit.*; see also Hunt (H.) and Briscoe, *J. Physical Chem.*, 1929, 33, 190, 1495; *J. Chem. Ed.*, 1929, 6, 1716. The importance of compound formation as a preliminary to

hydroxyl group is able to attach itself by covalent linkages to both anion and cation : the protective sheath formed in this way increases the effective size of the ions so that they cannot become associated in pairs in the way described by Bjerrum. Hydroxylic solvents may not only aid ionization in some instances, as shown above, but may also operate by preventing ion-association. Differentiating solvents are generally electron donors only and so can co-ordinate only with cations leaving the anions unsolvated, with the result that ion-pairs, as well as un-ionized molecules in certain cases, can exist.

A special type of solvent action is found in the influence on the behaviour of acids and bases : this subject will be considered more fully in the following chapter.

ionization in general is considered by Kendall *et al.*, *J. Amer. Chem. Soc.*, 1917, **39**, 2033, 2323 ; 1921, **43**, 1416 ; see also Fredenhagen, *loc. cit.* ; Ussanovitsch, *Acta Physicochim. U.S.S.R.*, 1935, **2**, 239. The conductance of nitro-compounds in liquid ammonia or in hydrazine (p. 6 *supra*) is undoubtedly preceded by compound formation.

ACID, BASE, AND SOLVENT EQUILIBRIA

$$\text{A} \rightleftharpoons \text{H}^+ + \text{B} \quad \text{. (i)}$$

acid proton base

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solvent S, assuming the activity of the latter to remain constant since it is always present in large excess, it follows that *

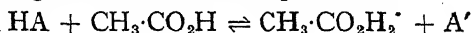
$$K_A = \frac{a_{HS} \cdot \times a_{A'}}{a_{HA}}$$

This equation is identical in form with that used earlier to define the dissociation constant of an acid HA, namely

$$K_a = \frac{a_{H^+} \cdot \times a_{A'}}{a_{HA}}$$

since the entity previously described as the 'hydrogen ion', the activity of which is written a_{H^+} and whose concentration is measured by *E.M.F.*, catalytic or indicator methods, is really the solvated ion HS^+ , as already explained. The new definition of an acid, therefore, requires no change of view in connection with the dissociation constant, except the realization of what is implied by the term hydrogen ion: as long as this is borne in mind it is still convenient to use the earlier expression and even to employ the symbols a_{H^+} and $[H^+]$ to represent the activity and concentration, respectively, of these ions.† Although the symbols are the same, the *actual ions* are, of course, different in different media, as indicated above.

Influence of Solvent—From what has been said, it is evident that a substance can only become acidic if dissolved in a medium the molecules of which are capable of taking up a proton: they are called 'protophilic' substances, and in addition to water and the alcohols, examples are acetone, ether and, to some extent, acetic and formic acids. When an acid HA is present in a medium, such as acetic acid, which is itself a strong proton donor, often called a 'protogenic' solvent, the equilibrium



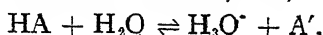
obviously cannot go very far to the right. The acid HA will therefore be weak, in the sense that the extent of ionization and the conductance will be smaller than for the corresponding acid in water; even acids like perchloric acid, which are highly ionized in an aqueous medium, appear to be dissociated only to a small extent

* Some writers prefer to define the dissociation constant of an acid in terms of the equilibrium $HA \rightleftharpoons H^+ + A^-$, where H^+ is a proton, so that $K = a_{H^+} a_{A^-} / a_{HA}$; this has the advantage of being a fundamental constant of the acid independent of the nature of the medium, but as nothing is known, even approximately, of a_{H^+} , the activity of the protons, the relationship has little practical value (see, however, p. 187.)

† In order to distinguish between real hydrogen ions in solution and protons, the un-solvated ions, the latter are written H^+ . In all future references to hydrogen ions, solvated ions, sometimes called by the general name 'lyonium ions', are to be understood.

in acetic acid.* It is a very striking fact, however, that the hydrogen ion activity in such solutions is exceptionally high, much higher than in aqueous solutions, so that they have been termed 'super-acid'.† This intense acidity has been demonstrated in a number of ways, e.g. by *E.M.F.*, by catalytic activity and by absence of lyolysis (*vide infra*) in salts of weak bases, although they are completely decomposed by water:‡ it is to be attributed to the fact that the $\text{CH}_3\text{CO}_2\text{H}_2^+$ ion has a very marked tendency to lose a proton. Super-acidity can only be observed, therefore, in strongly protogenic solvents, such as acetic and formic acids.

Another result of the small tendency for the molecule of acetic acid to hold a proton is that it is possible in such a solvent to differentiate between the strengths of acids such as perchloric, hydrobromic, hydrochloric and nitric, which are all 'strong acids' in water. On account of the strong protophilic tendency of the water molecule the ionization reaction, viz.,



goes virtually to completion for all the acids mentioned, and it is impossible to determine their relative strengths, except perhaps in very concentrated solutions.§ In a protogenic solvent, however, the interaction between the acid and solvent molecules is comparatively small, and the relative strengths of acids which appear equally strong in aqueous solution can be determined by conductivity,|| indicator,** *E.M.F.*,†† or catalytic ‡‡ methods: all these procedures give an approximate measure of the hydrogen ion concentrations. The results are in general agreement, showing decreasing strength in the order: $\text{HClO}_4 > \text{HBr} > \text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3$. In a strongly protophilic medium, such as liquid ammonia and possibly ether, it would be impossible to distinguish in strength between acids which can be easily differentiated in water: in a solvent of this type it is very probable that acetic and perchloric acids would appear to be equally strong!

Bases—In general the equilibrium between a solvent, which

* Kolthoff, *J. Amer. Chem. Soc.*, 1934, **56**, 1007; Weidner, Hutchison and Chandlee, *ibid.*, p. 1285 (other references in this paper).

† Hall (N. F.) and Conant, *ibid.*, 1927, **49**, 3047, 3062; Hall and Werner (T. H.), 1928, **50**, 2367; Conant and Werner (T. H.), *ibid.*, 1930, **52**, 4436; see also, Rodebush and Ewart, *ibid.*, 1932, **54**, 419.

‡ See also, Hammett and Dietz, *ibid.*, 1930, **52**, 4795.

§ Hantzsch and Weissberger, *Z. physikal. Chem.*, 1927, **125**, 251.

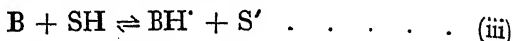
|| Kolthoff and Willman, *loc. cit.*

** Hantzsch and Voigt, *Ber.*, 1929, **62**, 975; see also Hammett *et al.*, *J. Amer. Chem. Soc.*, 1930, **52**, 4795; 1932, **54**, 4239; 1934, **56**, 827; Müller (A.), *Z. anorg. Chem.*, 1934, **217**, 113; **218**, 210.

†† Hall (N. F.) and Conant, *loc. cit.*; Hall and Werner, *loc. cit.*

‡‡ Hantzsch and Langbein, *Z. anorg. Chem.*, 1932, **204**, 193.

must be able to donate a proton and consequently be acidic to some extent, and a base * can be written



the solvent being here designated SH to indicate its acidic property. Applying the law of mass action, it follows that †

$$K_R = \frac{a_{BH'} \times a_{S'}}{a_B},$$

the activity of the solvent, since it is in excess, being taken as constant. This relationship is again identical with that generally used to define the dissociation constant of a weak base, especially in aqueous solution. Consider, for example, ammonia or an amine of the general formula $R \cdot NH_2$, then according to classical ideas the actual base is $R \cdot NH_3 \cdot OH$, and the dissociation constant, using concentrations instead of activities, is written

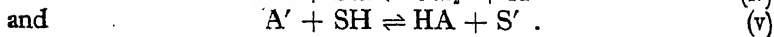
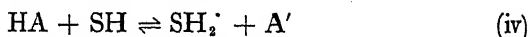
$$k_b = [R \cdot NH_3'] [OH'] / [R \cdot NH_3 \cdot OH].$$

In actual practice, however, the *whole* of the amine which is not ionized is assumed to be present as $R \cdot NH_3 \cdot OH$: ‡ that is to say, the basic dissociation constant as generally quoted is given by

$$k_b = [R \cdot NH_3'] [OH'] / [R \cdot NH_2].$$

Writing $R \cdot NH_2$ for the base B and H_2O for the solvent SH, it is at once evident that this equation is identical with that given above for K_B , based on the new definition of a base.§

Before proceeding further, it is of interest to consider the relationship between the dissociation constants of an acid and its conjugate base in the same solvent: the latter must, of course, be able easily both to accept and donate protons, that is to say it must be 'amphiprotic', as, for example, water and the alcohols. For the acid HA, the conjugate base is the anion A' , and if SH is the solvent, the acidic and basic equilibria are



respectively, and the dissociation constants are

$$K_A = a_{SH_2'} \times a_{A'} / a_{HA}$$

$$K_B = a_{HA} \times a_{S'} / a_{A'}$$

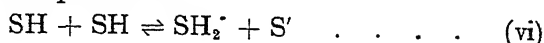
* It is assumed that the base is uncharged, but the arguments are equally applicable to one carrying a charge, e.g. acetate ion.

† The alternative dissociant constant, for the equilibrium $B + H^+ \rightleftharpoons BH^+$, involving actual protons is not used here (*vide supra*).

‡ See, however, Moore and Winmill, *J. Chem. Soc.*, 1912, 101, 1635.

§ The new concept does not preclude the presence of some hydrated base $R \cdot NH_3 \cdot OH$ in an aqueous solution of $R \cdot NH_2$: both are bases within the scope of the new definition.

where SH_2^+ is the hydrogen ion in the given medium and S' is the solvent anion. Since the solvent can itself function as either an acid or a base, the equilibrium



must exist in the solvent and in any solution in it; assuming the activity of the solvent molecules SH to remain constant it follows that

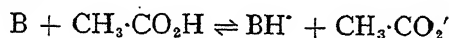
$$K_I = a_{\text{SH}_2^+} \times a_{\text{S}'} \quad \text{. (vii)}$$

the quantity K_I being called the **ionic product** of the solvent. From the three relationships for K_A , K_B and K_I it is seen that

$$K_B = K_I/K_A \quad \text{. (viii)}$$

and so the dissociation constant of a base is inversely proportional to that of its conjugate acid, and vice versa.

The strength of a base like that of an acid must depend on the nature of the solvent: in a protogenic medium like acetic acid the ionization process



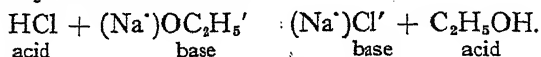
will take place to a very considerable extent even with bases which are weak in aqueous solution. Just as it is impossible to distinguish between the strengths of certain acids in water, so bases exceeding a particular strength should be indistinguishable in acetic acid: it has been found, in fact, that all bases stronger than aniline appear to be equally strong in acetic acid solution.* To arrange such bases in the order of their strengths it would be necessary to use a protophilic solvent, such as liquid ammonia or even ether: water is obviously better than acetic acid, but it is not possible to distinguish between the strong bases in the former, since they all produce OH' ions almost completely. It may be noted that in spite of the high degree of ionization which undoubtedly results when a base is dissolved in acetic acid, the solutions behave as weak electrolytes as far as the conductivity and the effect of dilution on the hydrogen ion concentration are concerned.† This anomaly is undoubtedly due to the very low dielectric constant of acetic acid, so that ion-pairs are formed to a considerable extent and there is only slight dissociation in spite of the great extent of ionization.

Neutralization and Lyolysis—In its widest sense the term neutralization should be applied to the reaction of one equivalent of an acid with one equivalent of a base, both acid and base being determined by the definitions already given. The products are, however, not to be described as a salt and a solvent molecule, but they are the conjugate base and acid, respectively, of the reacting

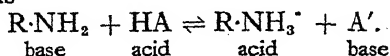
* Hall (N. F.), *J. Amer. Chem. Soc.*, 1930, 52, 5115; see also *Chem. Reviews*, 1931, 8, 191.

† Hall (N. F.) and Werner, *loc. cit.*

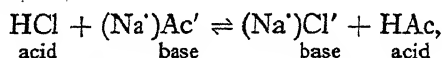
acid and base. For conventional acids, e.g. hydrochloric, acetic, etc., and 'lyate' bases, having their anion in common with the solvent, there is no fundamental difference between the new and classical points of view, the products being what is generally called a salt and a molecule of the solvent; for example, such a neutralization in ethyl alcohol would be



When an anhydro-base, e.g. ammonia or an amine, is neutralized the conjugate acid is the ammonium ion, and the base is the anion of the acid; thus

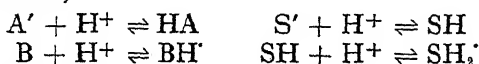


This process can occur in any medium, no water being involved although a salt, in the conventional sense, is formed. Other types of reaction which now fall into the category of neutralization are the so-called 'displacement' reactions, when a strong acid, e.g. hydrochloric acid, displaces a weak acid, e.g. acetic acid, from one of its salts, or when a strong base displaces a weak one. The reaction between sodium acetate and hydrochloric acid, for example, may be written

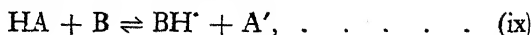


in which form it applies for any solvent: this is clearly a neutralization in the extended sense since the acetate ion is a base. Similarly the reaction between an alkali hydroxide and an ammonium salt is the neutralization of the ammonium ion acid by the hydroxyl ion base, the products being free ammonia (base) and water (acid).

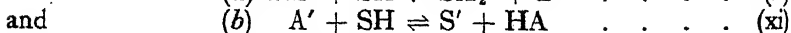
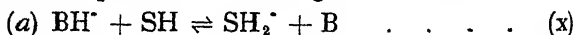
The extent to which the neutralization reaction occurs, when one equivalent of acid and base are mixed, depends on the nature of the acid, the base and the medium: if the acid is HA, the base is B, and the solvent is SH, as before, then if the latter is amphiprotic, four processes involving competition for protons co-exist in the solution,* viz.,



The neutralization reaction is to be written

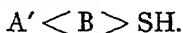


but owing to the fact that the solvent is itself capable of acting as a base and an acid, two processes involving the solvent



* Cf. Conant and Hall (N. F.), *J. Amer. Chem. Soc.*, 1927, **49**, 3062.

are possible which by re-forming the free base (B) and acid (HA) oppose the neutralization reaction. The processes (a) and (b), militating against complete neutralization, are called by the general name of **lyolysis**,* and in the particular case of water as solvent the term used is **hydrolysis**; this subject will be considered in some detail shortly. Considering the lyolysis reaction (a) it is seen that for this to take place to a small extent only, so that neutralization is virtually complete, it is necessary firstly that the proton affinity, i.e. basic strength, of the base B should be greater than that of the acid anion A' , so that the neutralization reaction goes considerably to the right, and secondly that it should be greater than that of the solvent, so that the lyolytic equilibrium (a) is almost entirely to the left. For complete neutralization, therefore, the order of basic strengths should be



If B is a weak base its proton affinity is small and lyolysis is considerable, unless A' is a still weaker base, that is to say the conjugate acid HA used in the neutralization must be very strong (see p. 179), and the solvent must also have a strongly acidic tendency. It has been found, in agreement with these conclusions, that extremely weak bases, e.g. acetoxime, can be neutralized completely by means of perchloric acid, the strongest known acid, in acetic and formic acid as solvents: † in water, of course, lyolysis is so considerable that neutralization is very small and the salts of acetoxime are only present to a minute extent. The so-called weak bases in water have a proton affinity which is less than that of water itself—this is, of course, implied by the term 'weak base'—so that neutralization can never be complete no matter how strong the acid: salts of weak bases are, therefore, said to be hydrolysed in water.

Considering the lyolytic equilibrium (b) it will be seen that for neutralization to be virtually complete it is necessary for the order of the *acid* strengths to be



To neutralize completely a weak acid HA it is therefore necessary to use a very strong base, so that its conjugate acid BH is extremely weak, and to work in a protophilic medium, such as ether, acetonitrile ‡ or, preferably, liquid ammonia. The so-called weak acids in aqueous solution are less protogenic than water in its acidic form

* The term in common use is 'solvolytic', but there are good reasons for preferring the word 'lyolysis', as suggested in a review of the first edition of this book (see *Trans. Faraday Soc.*, 1931, 27, 239).

† See, for example, Hall (N. F.) and Werner (T. H.), *loc. cit.*; Hammett and Dietz, *loc. cit.*

‡ Cf. Hantzsch, *Ber.*, 1931, 64, 667; Kilpatrick (M. L.) and Kilpatrick (M.), *Chem. Reviews*, 1933, 13, 131.

H_3O^+ ; hence salts of weak acids are all lyolysed (hydrolysed) to some extent in water.

It should be clear from what has been said that the lyolysis process (*a*) is due primarily to the weakness of the base B, whereas the process (*b*) results from the weakness of the acid. If both acid and base are weak in the particular solvent then both types of lyolysis can occur, and complete neutralization is only possible under suitable conditions in a medium which neither donates nor accepts protons: such solvents are considered below. In a medium which is a proton acceptor (protophilic) exclusively, then only the (*a*) type of lyolysis, namely that involving a weak base, is possible; weak acids should be completely neutralized provided a strong base is used. Similarly, in an exclusively proton-donating (protogenic) solvent,* only 'salts' of weak acids are lyolysed: strong acids should be completely neutralized even by weak bases.

An examination of the lyolytic equilibrium (*b*) shows that it is identical with equation (v) representing the basic functioning of the anion A' : when the acid is weak the equilibrium constant of the lyolysis (*b*), called the lyolytic (or solvolytic) constant, K_L , which is a measure of the extent to which lyolysis occurs (cf. p. 192), is thus given by

$$K_L = K_I/K_A, \quad \dots \dots \dots (\text{xii}a)$$

where K_A is the dissociation constant of the weak acid HA, the base B being strong. The degree of lyolysis thus depends on the ratio of the ionic product of the amphiprotic or protogenic solvent to the dissociation constant of the acid.† By examining the equation for the lyolysis of type (*a*) it will be seen that this is identical with the equation which represents the acidic function of the acid BH' in the solvent SH; it follows, therefore, that the lyolytic constant is equal to the acidic dissociation constant of BH' , and hence to the ratio of the ionic product of the solvent to the dissociation constant of the conjugate base B. Thus for the neutralization of a weak base,

$$K_L = K_I/K_B \quad \dots \dots \dots (\text{xii}b)$$

where K_B is the ordinary dissociation constant of the base. When both acid and base are weak then the two types of lyolysis occur simultaneously: adding the two equations, and substituting the values of K_A and K_B for HA and B, and K_I for the solvent, it follows that

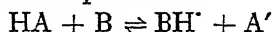
$$K_L = K_I/K_A K_B \quad \dots \dots \dots (\text{xii}c)$$

* Such solvents are rare: chloroform may possibly be one, but this is not certain, as it is generally supposed to be aprotic.

† It can be easily shown that K_L is also related to the ratio of the acidic dissociation constants of solvent and weak acid.

These are the fundamental equations of lyolysis which has been studied largely in aqueous media, to be considered shortly, and also to some extent in liquid ammonia, aniline, *p*-toluidine, formic acid, acetic acid and alcoholic solutions. As will be seen, the equilibrium can be considered from the standpoint of neutralization, or alternatively from a consideration of the extent of decomposition into acid and base when a 'salt' is dissolved in the given solvent.*

Aprotic Solvents—It is apparent that in a solvent which neither accepts nor donates protons, that is in an 'aprotic' medium, e.g. a hydrocarbon, a single substance can possess no appreciable acidic or basic function; nevertheless neutralization is possible in such media. If a proton donor and acceptor are added to benzene there will be a passage of protons from one to the other, so that neutralization occurs.† Since the solvent is neither protogenic nor protophilic, lyolysis is, of course, impossible, but neutralization will not necessarily be complete. Suppose the acid is HA and the added base is B, then the equilibrium



is set up, assuming, although it is not necessarily the case, that both HA and B are molecules without charge: applying the law of mass action it follows that

$$K = \frac{a_{\text{BH}'} \times a_{\text{A}'}}{a_{\text{HA}} \times a_{\text{B}}}$$

The fundamental dissociation constant of the acid HA into A' ions and protons, K_{HA} , is $a_{\text{A}'} \times a_{\text{H}^+}/a_{\text{HA}}$, and that for the acid BH', the conjugate of the base B, is given by $K_{\text{BH}'} = a_{\text{B}} \times a_{\text{H}^+}/a_{\text{BH}'}$; it is evident, therefore, that

$$K = K_{\text{HA}}/K_{\text{BH}'}$$

The extent of neutralization thus depends on the dissociation constants of the neutralized acid and of the conjugate acid corresponding to the base used: the larger the value of the former the more complete is the neutralization. If the colour of the base B is different from that of its conjugate acid BH', that is to say if the substance is an 'indicator', it is possible to determine the ratio of the dissociation constants $K_{\text{HA}}/K_{\text{BH}'}$ from the colour attained.

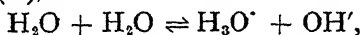
* See, for example, Franklin, *ibid.*, 1905, 27, 820 (ammonia); Schlesinger, *ibid.*, 1911, 33, 1932 (formic acid); Williams (R. J.) and Truesdail, *ibid.*, 1923, 45, 1348 (alcohol); Nadeau and Branchen, *ibid.*, 1935, 57, 1363 (acetic acid); Kolthoff, *J. Physical Chem.*, 1931, 35, 2732 (alcohol); Goldschmidt *et al.*, *Z. physikal. Chem.*, 1921, 99, 116; 1924, 112, 423; 1926, 119, 439 (alcohols); 1929, 143, 354 (amines); also references to Hall, Hammett, etc., already given.

† La Mer and Downes, *J. Amer. Chem. Soc.*, 1931, 53, 888; 1933, 55, 1840.

In this way the strengths of a series of acids can be compared.* It may be noted that since the aprotic solvent plays no part in the functioning of the acid or base, the levelling effect observed in other solvents when a certain strength is exceeded does not occur; in such a solvent it should thus be possible, theoretically at least, to arrange *all* acids and bases according to their strengths.

Ionic Equilibria in Water—Neutralization and lyolytic equilibria have hitherto been discussed from a general point of view, but since aqueous solutions are the most common and have been studied very thoroughly, the equilibria in water will be considered in more detail. The treatment given here can be readily adapted to any other solvent of an amphiprotic character without difficulty, but with media which are either exclusively protogenic or protophilic it must be remembered that only one type of lyolysis is possible in each case (p. 186).

The ionic equilibrium for water, corresponding to the general case of equation (vi), is



so that the ionic product of water, assuming the activity of unionized water molecules to be constant, is given by

$$\begin{aligned} K_w &= a_{\text{H}_3\text{O}^+} \times a_{\text{OH}^-} \\ &= [\text{H}_3\text{O}^+] [\text{OH}^-] f_{\text{H}_3\text{O}^+} f_{\text{OH}^-} \end{aligned}$$

where the f terms represent the activity coefficient of the species indicated. If the activity coefficients of the ions are assumed to be unity,† as they will be in very dilute solutions, the relationship for the ionic product becomes

$$[\text{H}^+] [\text{OH}^-] = k_w$$

it being understood that $[\text{H}^+]$ refers to the concentration of H_3O^+ ions, for hydrogen ions in water exist in that form. Since k_w is of the nature of an equilibrium constant it will vary with the temperature, but under ordinary conditions (15° – 25°) its value may be taken as about 10^{-14} , with concentrations expressed in gm. ions per litre. This value should hold in pure water and in dilute aqueous solutions, although not necessarily in concentrated solutions.

In an exactly neutral solution, or in perfectly pure water, the hydrogen and hydroxyl ion concentrations‡ are equal; hence under these conditions

$$[\text{H}^+] = [\text{OH}^-] = \sqrt{k_w} = 10^{-7} \text{ gm. ions per litre.}$$

* Brønsted, *Ber.*, 1928, 61, 2049; La Mer and Downes, *loc. cit.* (1933); see also Hantzsch and Voigt, *loc. cit.*

† The limitations of this assumption will be considered later, p. 213.

‡ Strictly speaking activities should be employed, but in dilute solutions activities and concentrations are almost identical, and as the concept of concentration is the simpler and has a more definite physical significance it may be used here.

At ordinary temperatures, therefore, the hydrogen and hydroxyl ion concentrations in a neutral solution are approximately 10^{-7} gm. ions per litre; in an acid solution $[H^+]$ is greater than 10^{-7} , but $[OH^-]$ is less, and in alkaline solution $[H^+]$ is less than 10^{-7} , but $[OH^-]$ is greater than this amount.

Hydrogen Ion Exponents (pH)—Hydrogen ion concentrations play an important part in various aspects of chemistry* and a convenient method of expressing these concentrations was suggested by Sørensen.† The *negative* logarithm of the hydrogen ion concentration is called the ' pH ' ‡ of the solution; thus

$$pH = -\log_{10} [H^+] = \log_{10} \frac{1}{[H^+]} \quad (\text{xiii})$$

or

$$[H^+] = 10^{-pH}.$$

According to this convenient form of expression the pH of a neutral solution is equal to 7, since $[H^+] = 10^{-7}$; in an acid solution the pH is less than, and in an alkaline solution greater than, 7. It is important to remember that the greater the hydrogen ion concentration the smaller is the pH .‡

The logarithmic, or exponential, method has been found useful not only for expressing concentrations but also for other numerical quantities, e.g. dissociation constants, which cover a large range of magnitudes. Thus hydroxyl ion concentrations are written in terms of pOH , where

$$pOH = -\log [OH^-], \quad \dots \quad (\text{xiv})$$

and dissociation constants are expressed as pK , which is equal to $-\log K$. Thus the equation

$$[H^+] [OH^-] = K_w = 10^{-14}$$

may be written in the form

$$\log [H^+] + \log [OH^-] = \log K_w = -14$$

$$\therefore pH + pOH = pK_w = 14 \quad \dots \quad (\text{xv})$$

* See Clark (W. M.), *The Determination of Hydrogen Ions*; Britton, *Hydrogen Ions*.

† *Compt. rend. Lab. Carlsberg*, 1909, 8, 1; *Biochem. Z.*, 1909, 21, 131, 201.

‡ Sometimes written P_H , p_H or p^+H . Ideally pH should perhaps be defined as $-\log a_{H^+}$, where a_{H^+} is the activity of the appropriate hydrogen ions. Nearly all so-called hydrogen ion concentrations are based on determinations made by *E.M.F.* methods, and really represent *mean* activities of the ions in the solution. It is admittedly an approximation to speak of an experimental pH as a measure of hydrogen ion *concentration*, but it is also unjustifiable to regard it as a measure of the activity of these ions. The subject is considered in some detail by Clark, *op. cit.*, 1928, p. 461; and by Kolthoff, *Rec. trav. chim.*, 1930, 49, 401. True hydrogen ion concentrations can be determined in certain cases by *E.M.F.* or catalytic methods (for references, see p. 200).

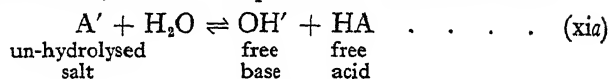
This relationship should hold for all dilute aqueous solutions at ordinary temperatures.

It will be seen later that when an acid has been 'neutralized' by an equivalent amount of a base, i.e. at the so-called 'equivalence point', the solution is by no means always neutral, in the sense that the pH is 7. A solution of this hydrogen ion concentration may be regarded as a reference point for differentiating between acidity and alkalinity. It is important to remember that the pH of a neutral solution depends on the value of k_w , and the latter varies with temperature (p. 211) and with the nature of the solution (p. 213); to regard an electrolyte of pH 7 as neutral is, therefore, a convenient approximation for dilute aqueous solutions at ordinary temperatures.

Hydrolysis of Salts.—Case 1. Salt of Strong Base and Weak Acid—It has been seen (p. 185) that when a weak acid (HA) is neutralized by a strong base in a protogenic solvent (SH), then on account of the acidic nature of the solvent lyolysis occurs which tends to make neutralization incomplete; thus

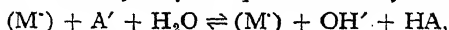


If the solvent is water, then the equilibrium takes the form



and the process is known as **hydrolysis**. The equation (xia) implies that on account of the weakness of the acid HA, there is a tendency for its anions (A') to take up protons from the water, which is capable of acting as an acid, thus forming un-ionized molecules of HA. When a salt MA is dissolved in water it dissociates almost completely into M' and A' ions, and the latter immediately interact with the molecules of water to form HA molecules and OH' ions: * the result is, therefore, a re-formation of the original acid and the base OH' , that is to say, there is a partial reversal of neutralization.† As a result of the formation of hydroxyl ions the pH of

* The conventional method of considering hydrolysis is that the water ionizes into H' (really H_3O') and OH' ions, and that owing to the weakness of the acid HA, there is a tendency for the H' ions to unite with some of the A' ions produced by ionization of the salt MA; on the other hand, since the base is strong, the ions M' and OH' can co-exist without any tendency to unite. The hydrolytic equilibrium may then be written:



which is identical with equation (xia).

† Hydrolysis is often defined as partially reversed neutralization when a salt is dissolved in water, although it would perhaps be better to consider lyolysis in general as incomplete neutralization due to interaction with the solvent, because of the ability of the latter to function as an acid or base.

the solution of a salt of a weak acid and strong base is greater than 7; that is to say, it reacts alkaline.

Applying the law of mass action to equation (xi_a), assuming the activity of the water to be constant, as it will be in dilute solutions, it follows that

$$K_h = \frac{a_{\text{OH}'} \times a_{\text{HA}}}{a_{\text{A}'}} = \frac{[\text{OH}'] [\text{HA}]}{[\text{A}']} \cdot \frac{f_{\text{OH}'} f_{\text{HA}}}{f_{\text{A}'}} \quad (\text{xvi})$$

Since the concentration of HA is very small the activity coefficient may be taken as unity,* and so

$$K_h = \frac{[\text{OH}'] [\text{HA}]}{[\text{A}']} \cdot \frac{f_{\text{OH}'}}{f_{\text{A}'}} \quad (\text{xvii})$$

This is the accurate expression for K_h , the hydrolysis constant, but in the majority of cases considered the solution of the salt is so dilute that $f_{\text{OH}'}/f_{\text{A}'}$, may be considered as unity (cf. Chap. VII, equation xxiii); † equation (xvii) then reduces to the approximate form

$$k_h = \frac{[\text{OH}'] [\text{HA}]}{[\text{A}']} \quad (\text{xviii})$$

which is really only applicable in dilute solutions and in the absence of a large concentration of other ions. The salt remaining unhydrolysed when equilibrium is attained and the free strong base formed are almost completely dissociated, and so their concentrations may be taken as equivalent to $[\text{A}']$ and $[\text{OH}']$ respectively; the free acid produced by hydrolysis is almost completely in the un-ionized form, and so its concentration may be regarded as $[\text{HA}]$; hence equation (xviii) can be written in the form:

$$k_h = \frac{\text{Concentration of Free Base} \times \text{Concentration of Free Acid}}{\text{Concentration of Un-hydrolysed Salt}} \quad (\text{xix})$$

The hydrolysis constant is related in the following manner to the 'degree of hydrolysis', i.e. the fraction of each gm. mol. of salt hydrolysed when equilibrium is attained, at any dilution. Consider a solution of the salt MA at a concentration of c gm. mol. per litre, and suppose x is the degree of hydrolysis at equilibrium; the solution will then contain:

* This is justifiable in dilute solution, since HA is uncharged; in concentrated salt solutions the activity coefficient may be greater than unity on account of the 'salting-out' effect.

† The case is rather more complicated if A is not a univalent ion; the equation then involves $f_{\text{OH}'}^n/f_{\text{A}'}^n$, where n is the valency of the ion A' . According to the Debye-Hückel equations (p. 142), this is not unity even in dilute solutions; for very dilute solutions, however, when the ionic strength is small, the error will not be appreciable.

- (a) $(1 - x)c$ gm. mols. of almost completely dissociated un-hydrolysed salt MA, i.e. $(1 - x)c$ gm. ions of each M' and A' ,
 (b) xc gm. mols. of almost completely un-ionized weak acid HA, and
 (c) xc gm. mols. of almost completely dissociated strong base MOH, i.e. xc gm. ions of each M' and OH' ,
 per litre. It is therefore possible to write

$$[OH'] = xc; [HA] = xc \text{ and } [A'] = (1 - x)c$$

$$k_h = \frac{[OH'] [HA]}{[A']} = \frac{xc \times xc}{(1 - x)c} = \frac{x^2 c}{1 - x} \quad (xx)$$

Solving the quadratic equation for x , it is found that

$$= -\frac{k_h}{2c} + \sqrt{\frac{k_h^2}{4c^2} + \frac{k_h}{c}} \quad (xxi)$$

and the degree of hydrolysis at any concentration c may be determined if the hydrolytic constant is known.* If k_h is small, this expression reduces to

$$x \approx \sqrt{k_h/c} \quad (xxii)^\dagger$$

The degree of hydrolysis of a given salt is thus roughly proportional to the square-root of the hydrolysis constant, and inversely proportional to the square-root of the concentration. The value of k_h increases markedly with temperature, and so also does the extent of hydrolysis of the salt: this must also increase with decreasing concentration of the solution, that is as it is made more dilute. Since the relationships $[H'] [OH'] = k_w$ for water, and

$$[H'] [A']/[HA] = k_a$$

for the weak acid must hold in the same solution as the hydrolytic equation,

$$\frac{[OH'] [HA]}{[A']} = k_h,$$

it follows that

$$k_h = k_w/k_a \quad (xxiii)$$

This equation is identical with the corresponding form of the more general equation (xii a) deduced on p. 186. Writing this relationship in the logarithmic form, it follows that

$$p k_h = p k_w - p k_a \quad (xxiv)$$

The hydrolytic constant is thus related to the ionic product of

* For a more accurate treatment, especially when hydrolysis is considerable, allowance should be made for the ionization of the weak acid; compare the case of a salt of a weak acid and a weak base, p. 198 *infra*. See also Bjerrum, *Ahren's Sammlung*, 1914, No. 21.

† The same result may be obtained by assuming that x is small, when $1 - x \approx 1$, in equation (xx).

water, and the dissociation constant of the acid. Substituting for k_h in the approximate equation

$$x = \sqrt{k_h/c}$$

it follows that

$$x = \sqrt{k_w/k_a c} \quad \dots \quad (xxv)$$

If two salts are compared at the same concentration the degree of hydrolysis of each is inversely proportional to the square root of the dissociation constant of the weak acid; hence the weaker the acid the greater the extent of hydrolysis. The figures given in Table XXVIII illustrate this point.

TABLE XXVIII

DEGREES OF HYDROLYSIS FOR VARIOUS STRENGTHS OF ACID AND SALT CONCENTRATIONS (18°)

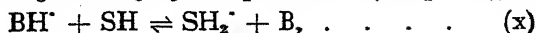
k_a	k_h	Concentration of Solution.			
		0.001N	0.01N	0.1N	N
10^{-4}	10^{-10}	3.3×10^{-4}	10^{-4}	3.2×10^{-5}	10^{-5}
10^{-6}	10^{-8}	3.2×10^{-3}	10^{-3}	3.2×10^{-4}	10^{-4}
10^{-8}	10^{-6}	0.032	0.01	3.2×10^{-3}	10^{-3}
10^{-1}	10^{-4}	0.27	0.095	0.032	10^{-2}

The hydrogen ion concentration of a solution of a hydrolysed salt may be readily calculated by the use of equation (xxv);* since

$$\begin{aligned} & [\text{OH}'] = xc \\ \text{and } & [\text{H}'] [\text{OH}'] = k_w \\ & \therefore [\text{H}'] = k_w/xc \\ & \therefore [\text{H}'] = k_w/c \sqrt{k_w/k_a c} = \sqrt{k_w k_a/c} \quad \dots \quad (xxvi) \\ & \therefore pH = \frac{1}{2}pk_w + \frac{1}{2}pk_a + \frac{1}{2} \log c \quad \dots \quad (xxvii) \end{aligned}$$

It is clear, therefore, that the pH, or alkalinity, of the solution increases with concentration, although the degree of hydrolysis decreases. Increase of temperature causes a marked increase in k_w (p. 211), but generally has little effect on k_a ; hence k_h and the degree of hydrolysis of a salt invariably increase as the temperature is raised.

Case 2. Salt of a Weak Base and Strong Acid—On account of the basic nature of the solvent and the weakness of the base involved in the salt, the former is an effective competitor for the protons available from the acid, so that for a salt of the type under consideration the general lyolytic equilibrium (see p. 184) is

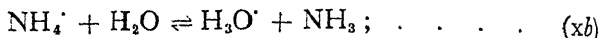


and where water is the solvent it is written

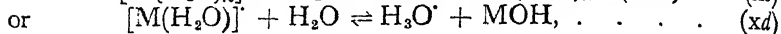
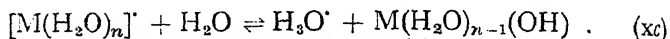


* For a more accurate treatment of this subject, see Bjerrum (*op. cit.*); cf. also Jeffery, Vogel (A. I.) and Lowry (H. V.), *J. Chem. Soc.*, 1933, 1637; Kilpi, *Z. physikal. Chem.*, 1935, 172, 277.

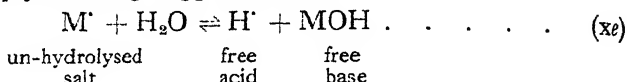
An equation of this type covers the hydrolysis of an ammonium, or similar, salt, in which the weak base B is NH_3 , thus



but when the base is a metallic hydroxide, the hydrolysis must be written



or more simply, although approximately,



where the hydrogen ion is certainly, and the metal ion probably, hydrated. The hydrolytic equilibrium of the salt of a strong acid and weak base is generally written in the form of equation (xe), and provided it is realized that M^+ may represent possibly an unhydrated ion, but also, more probably, an aquo-ion, e.g. $[\text{M}(\text{H}_2\text{O})_n]^+$, or an acidic cation of the type BH^+ , this equation may be regarded as applicable to all cases of hydrolysis. It implies that when a salt of a weak base is dissolved in water a reaction occurs in which some of the cations unite with the hydroxyl ions from the water to form un-ionized molecules of base, leaving an equivalent amount of free hydrogen ions.* The latter cause the pH of the solution to fall below the value of 7, and so it reacts acid.

By applying the law of mass action to equation (xe), in a manner similar to that adopted for the hydrolytic equilibrium with the salt of a strong base and weak acid, the following equations may be obtained :

$$k_h = \frac{[\text{H}^+][\text{MOH}]}{[\text{M}^+]} = \frac{k_w}{k_b} \quad \dots \quad (\text{xxviii})$$

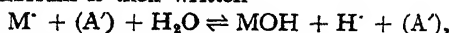
$$= \frac{x^2c}{1-x} \quad \dots \quad (\text{xxix})$$

and also

$$k_h = \frac{\text{Concentration of Free Base} \times \text{Concentration of Free Acid}}{\text{Concentration of Un-hydrolysed salt}} \quad (\text{xxx})$$

$$\text{Further,} \quad \sqrt{k_h/c} = \sqrt{k_w/k_b c} \quad (\text{xxxi})$$

* In the conventional treatment of hydrolysis it is supposed that owing to the weakness of the base MOH, some of the M^+ ions from the salt MA unite with OH^- resulting from the ionization of water to form un-ionized MOH, whereas H^+ and A^- can co-exist since the acid is a strong one. The hydrolytic equilibrium is then written



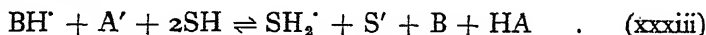
and so is identical with equation (xe) above.

$$\text{and} \quad [\text{H}'] = xc = \sqrt{k_w c / k_b} \quad . \quad . \quad . \quad (\text{xxxii})$$

$$p\text{H} = \frac{1}{2}pK_w - \frac{1}{2}pK_b - \frac{1}{2} \log c \quad . \quad (\text{xxxiii})$$

As in the previous case, the degree of hydrolysis of a given salt increases with dilution and with temperature; at a given dilution a salt is more hydrolysed the weaker the base of which it is composed.

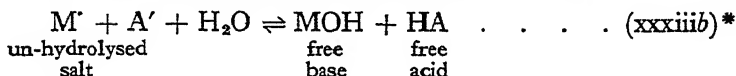
Case 3. Salt of Weak Base and Weak Acid—With a salt resulting from the neutralization of a weak base by a weak acid the hydrolysis in the general case is represented by adding equations (x) and (xi), since both acidic and basic functions of the solvent are operative; thus



and for water this becomes



or in the simplest form for the salt MA of a weak acid HA and a weak base MOH, by adding equations (xi*a*) and (x*e*),



the equilibrium $\text{H}' + \text{OH}' \rightleftharpoons \text{H}_2\text{O}$ being eliminated. The wider significance of M' referred to in connection with the salt of a strong acid and weak base (p. 194) is equally applicable here. In this case there is no appreciable excess of hydrogen or hydroxyl ions, and, in fact, if the dissociation constants of acid and base were equal, the solution would be exactly neutral, i.e. pH 7. If the dissociation constant of the acid is greater than that of the base, e.g. with ammonium benzoate, the solution will be slightly acid, but if the reverse is true, e.g. ammonium carbonate, the solution becomes alkaline. Although hydrolysis is frequently accompanied by the development of an acid or an alkaline reaction in water, it should be evident that this can only occur when either the acid or the base is definitely stronger than the other.

If, as in the previous cases, the law of mass action is applied to the hydrolytic equilibrium represented by equation (xxxiii*b*), it follows that

$$K_h = \frac{a_{\text{MOH}} \times a_{\text{HA}}}{a_{\text{M}'} \times a_{\text{A}}} \quad . \quad . \quad . \quad (\text{xxxiv})$$

the activity of the un-ionized water being taken as constant. Re-

* In the conventional deduction of this equation it is supposed that when the salt MA is dissolved in water some of the M' ions combine with the OH' from the water to form un-ionized MOH, and the A' ions unite with H' to give un-ionized HA, since both acid and base are weak. Equation (xxxiii*b*) then follows directly for the hydrolytic equilibrium.

placing activities by actual concentrations and activity coefficients,

$$K_h = \frac{[\text{MOH}][\text{HA}]}{[\text{M}'][\text{A}']} \cdot \frac{f_{\text{MOH}} f_{\text{HA}}}{f_{\text{M}'} f_{\text{A}'}} \quad (\text{xxxiv})$$

In dilute solution the activity coefficients of the un-ionized molecules, i.e. f_{MOH} and f_{HA} , may be taken as unity; further, $f_{\text{M}'} \times f_{\text{A}'} = f_{\pm}^2$, where f_{\pm} is the mean activity coefficient of the salt, then

$$K_h = \frac{[\text{MOH}][\text{HA}]}{[\text{M}'][\text{A}']} \cdot \frac{1}{f_{\pm}^2} \quad (\text{xxxv})$$

This is the accurate expression for the hydrolysis constant of a salt of two-sided weakness; in practice f_{\pm} is generally taken as unity, and the approximate equation

$$k_h = \frac{[\text{MOH}][\text{HA}]}{[\text{M}'][\text{A}']} \quad (\text{xxxvi})$$

is obtained. In concentrated solutions, or in the presence of neutral salts or other electrolytes, the values of k_h calculated from this formula would not be constant, as the activity coefficient of the salt, which is a function of the ionic strength, would certainly be less than unity; in any case it would not be the same as in dilute solution.

Since the acid HA and base MOH may be regarded as almost completely un-ionized, and the salt MA as completely dissociated into M' and A' ions, the approximate form of the hydrolysis constant expression may be written as:

$$k_h = \frac{[\text{MOH}][\text{HA}]}{[\text{M}'][\text{A}']} \cdot \frac{\text{Concentration of Base} \times \text{Concentration of Acid}}{(\text{Concentration of Un-hydrolysed salt})^2} \quad (\text{xxxvii})$$

As in case I, the expressions

$$k_w = [\text{H}'][\text{OH}']$$

$$k_a = \frac{[\text{H}'][\text{A}']}{[\text{HA}]} \quad \text{and} \quad k_b = \frac{[\text{M}'][\text{OH}']}{[\text{MOH}]}$$

hold simultaneously with the expression for hydrolytic equilibrium, hence

$$k_w/k_a k_b = k_h \quad (\text{xxxviii})$$

This equation is exactly the same as that deduced for the general case of lyolysis with a weak acid and a weak base (equation xii, p. 186). The logarithmic form of equation (xxxviii) becomes

$$p k_h = p k_w - p k_a - p k_b \quad (\text{xxxix})$$

If the original concentration of the solution is c gm. mols. per

litre, and a fraction x is hydrolysed, then when hydrolytic equilibrium is established the solution contains :

(a) $(1-x)c$ gm. mols. per litre of almost completely dissociated un-hydrolysed salt MA, i.e. $(1-x)c$ gm. ions per litre of each M' and A' ,

$$\therefore [M'] = [A'] = (1-x)c,*$$

(b) xc gm. mols. per litre of almost un-ionized weak acid HA,

$$\therefore [HA] = xc,$$

and (c) xc gm. mols. per litre of almost un-ionized weak base MOH,

$$\therefore [MOH] = xc.$$

$$\text{Hence } k_h = \frac{[HA][MOH]}{[M'][A']} = \frac{x^2}{(1-x)^2} \quad (\text{xI})$$

$$\text{or } x = \frac{\sqrt{k_h}}{1 + \sqrt{k_h}} \quad (\text{xli})$$

If k_h is small, it may be neglected in comparison with unity,

$$\therefore k_h:$$

$$\text{and } \sqrt{k_h} = \sqrt{\frac{k_w}{k_a k_b}} \quad (\text{xlii})$$

The expressions for x indicate that the degree of hydrolysis is independent of the concentration of the salt MA, but depends solely on the dissociation constants of the constituent acid and base. This conclusion is only, however, approximately true, as will be indicated shortly.

The hydrogen ion concentration of the hydrolysed salt solution may be readily calculated :

$$[H'] = k_a \frac{[HA]}{[A']} = k_a \frac{xc}{(1-x)c} = k_a \frac{x}{1-x}$$

$$\text{But } \sqrt{k_h} = \frac{x}{1-x}$$

$$\therefore [H'] = k_a \sqrt{k_h} = \sqrt{k_w k_a / k_b} \quad (\text{xliii})$$

$$\text{or } pH = \frac{1}{2}pk_w + \frac{1}{2}pk_a - \frac{1}{2}pk_b \quad (\text{xliv})$$

If $k_a = k_b$, that is the dissociation constants of acid and base are equal, then $[H'] = \sqrt{k_w} = 10^{-7}$ gm. ions per litre, and the solution is neutral, *although hydrolysis may be considerable*. On the other hand if $k_a > k_b$, $[H'] > 10^{-7}$ and the solution is acid, but when $k_a < k_b$, the solution is alkaline.

* It is assumed that the base and acid do not contribute any M' or A' ions.

Since the equation for hydrogen ion concentration contains no reference to the concentration, it follows that $[H^+]$, like the degree of hydrolysis, is roughly independent of the concentration of the solution.* It has been pointed out, however,† that in very dilute solutions, e.g. 1 gm. mol. in 5,000 litres, the weak acid and base have an appreciable ionization which must be considered. Under these conditions $[HA]$ and $[MOH]$, on the one hand, and $[M^+]$ and $[A^-]$ on the other, are not necessarily equal; in fact equality will only result if $k_a = k_b$, and this is a rare occurrence. The hydrogen ion concentration of the solution may, however, be calculated if k_a , k_b and k_w are known. In the dilute solution considered the salt will be completely dissociated, and hence

$$[A^-] + [HA] = c \quad \text{. (xlv)}$$

and
$$[M^+] + [MOH] = c \quad \text{. (xlvi)}$$

since the whole of the salt is either in the form of ions or free acid (or base). Further, as the solution must be electrically neutral,

$$[H^+] + [M^+] = [A^-] + [OH^-] \quad \text{. (xlvii)}$$

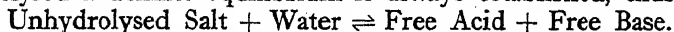
By means of these equations, and those for k_a , k_b , and k_w , it is possible to calculate $[H^+]$ for various dilutions. Thus for aniline acetate Griffith obtained the following results :

50 litres per gm. mol.	$[H^+] = 2.17 \times 10^{-5}$	gm. ions per litre
500 " " "	2.13×10^{-5}	" " " "
5,000 " " "	1.79×10^{-5}	" " " "

It is clear, therefore, that the variation in hydrogen ion concentration only becomes appreciable at high dilutions.

In concentrated solutions deviations are also to be expected, but for an entirely different reason. The constancy of $[H^+]$ is bound up with that of k_h , and the latter, as already mentioned, varies with the ionic strength of the solution; this variation is considerable at high concentrations.

Displacement of Hydrolytic Equilibrium—When a salt is hydrolysed a definite equilibrium is always established, thus :



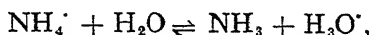
This equilibrium can be displaced in either direction by altering the concentrations of the products of hydrolysis. The addition of either the free acid or the free base will increase the concentration of un-hydrolysed salt, i.e. the degree of hydrolysis is decreased; the hydrolysis of sodium phenoxide, for example, is reduced by the addition of either phenol or sodium hydroxide. The repression of the hydrolysis of aniline hydrochloride by the addition of aniline has been made use of in a method for investigating the degree of

* Tizard, *J. Chem. Soc.*, 1910, 97, 2494.

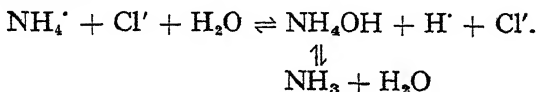
† Griffith, *Trans. Faraday Soc.*, 1922, 17, 525.

hydrolysis of the salt (p. 202). If the acid component of a salt is weak the addition of any alkali—actually OH' ions—will diminish hydrolysis; similarly, any acid—actually H' ions—will reduce the hydrolysis when the base is weak. A salt of two-sided weakness, e.g. ammonium acetate, can only have its hydrolysis decreased by the addition of its own constituent acid or base, i.e. acetic acid or ammonium hydroxide.

If, on the other hand, the free acid or base can be removed from the sphere of reaction the degree of hydrolysis will be increased, since more salt must hydrolyse to maintain the equilibrium. A solution of ammonium chloride is faintly acid owing to hydrolysis, thus :



or the hydrolytic equilibrium may be represented in the more conventional form :



On boiling the ammonia volatilizes more readily than the hydrochloric acid; hence the equilibrium is displaced to the right, and after a time the solution becomes definitely acid in reaction. The bases resulting from hydrolysis are often sparingly soluble, and their solubility products may be exceeded before hydrolytic equilibrium is reached; in such cases considerable hydrolysis will occur, until the acid has accumulated to a sufficient extent to compensate for the low concentration of the base. The marked hydrolysis of ferric chloride is probably due to such behaviour; the ferric hydroxide does not, however, form a visible precipitate, but remains in colloidal solution. The addition of hydrochloric acid to this brown colloidal solution decreases the degree of hydrolysis of the ferric chloride, and the solution becomes yellow—the normal colour of a solution of ferric ions.

A solution of the salt of a weak base has an excess of hydrogen ions, and one of the salt of a weak acid an excess of hydroxyl ions; if two such solutions are mixed the hydrogen and hydroxyl ions will unite, and be removed to form un-ionized water, and so the degree of hydrolysis of each salt must increase. The resulting solution is, in fact, equivalent to one containing the salt of a weak acid and a weak base; such salts are considerably hydrolysed. The addition of ammonium chloride to sodium aluminate is an example of this behaviour; the degree of hydrolysis of the latter is increased to such an extent that aluminium hydroxide is precipitated.*

* For applications of hydrolytic phenomena in analytical chemistry, see Bassett, *The Theory of Quantitative Analysis*.

In determining the conductivity of a salt of a weak acid or of a weak base the effect of hydrolysis is serious, since the free hydrogen or hydroxyl ions produced have such high conductances. In their work on sodium acetate, MacInnes and Shedlovsky* added a small excess of acetic acid, so as to repress hydrolysis, and applied a correction for the conductance of this excess: incidentally the acetic acid represses the ionization of the carbonic acid present in equilibrium conductivity water and so makes its effect negligible. An alternative method in which allowance is made for the hydrolysis of the salt of a weak acid by calculating the hydrogen ion concentration has also been used.†

Case 4. Salt of Strong Acid and Strong Base—From the discussion on p. 185 it is clear that if a strong acid is neutralized by a strong base the process is virtually complete, and so when the salt of such an acid and base is dissolved in water hydrolysis is insignificant. There is no tendency for the anions to combine with protons nor of the cations to give up protons, or to combine with hydroxyl ions. A solution of this type has an almost neutral reaction, and the pH is about 7 when the salt is dissolved in pure water.

Determination of Degree of Hydrolysis and Hydrolytic Constants.‡—**Reaction Velocity Methods**—Certain reactions, e.g. the hydrolysis of esters, and the inversion of cane sugar, are catalysed by hydrogen ions; the velocity constants are then roughly proportional to the concentration of these ions.§ If the velocity constant is determined in a solution of known hydrogen ion concentration, then the approximate values in other solutions may be calculated from velocity measurements in those solutions. The use of this general idea for investigating the hydrolysis of salts was first suggested by Walker,|| and applied by him, and by others.**

* *J. Amer. Chem. Soc.*, 1932, 54, 1429.

† Vogel (A. I.) *et al.*, *J. Chem. Soc.*, 1933, 1637; 1935, 21.

‡ For reviews, see Farmer, *Brit. Assoc. Reports*, 1901, 240; Naumann and Rücker, *J. prak. Chem.*, 1906, 74, 209; Lundén, *Ahrens's Sammlung*, 1908, No. 14.

§ It has been previously indicated (p. 101) that anions and even unionized molecules are often catalytically active, and so the proportionality can only be very approximate; by using appropriate reactions, however, satisfactory hydrogen ion concentrations may be determined in this way. See Brønsted and Grove, *J. Amer. Chem. Soc.*, 1930, 52, 1394; Kilpatrick (M.) *et al.*, *ibid.*, 1931, 53, 1732; 1934, 56, 2051.

|| *Z. physikal. Chem.*, 1889, 4, 319.

** Walker *et al.*, *J. Chem. Soc.*, 1895, 67, 576; *ibid.*, 1903, 83, 484; Ley, *Z. physikal. Chem.*, 1899, 30, 218; Bruner, *ibid.*, 1900, 32, 133; Carrara and Vespignani, *Gazz.*, 1900, 30, 35; Kahlenberg, Davis and Fowler, *J. Amer. Chem. Soc.*, 1899, 21, 1; Lundén, *Z. physikal. Chem.*, 1906, 54, 532; Johnston, *Proc. Roy. Soc.*, 1906, 78 A, 82; Cumming, *ibid.*, p. 103; Tansley, *J. Chem. Soc.*, 1923, 123, 3164.

The chief reactions used were the hydrolysis of methyl acetate, and the inversion of cane sugar, when studying salts of strong acids and weak bases. If the hydrogen ion concentration of the salt solution is known the hydrolytic constant and the degree of hydrolysis may be readily calculated. Thus

$$[\text{H}^+] = xc \quad \therefore x = [\text{H}^+]/c$$

$$\text{and} \quad k_h = \frac{x^2 c}{1 - x} = \frac{[\text{H}^+]^2}{c - [\text{H}^+]} \quad \dots \quad (\text{xlvi})$$

In studying the hydrolysis of the salt of a weak acid, a reaction which is influenced by hydroxyl ions is necessary; the decomposition of nitroso-triacetoneamine,* the mutarotation of glucose,† and the conversion of diacetone alcohol into acetone ‡ are all applicable. Since the rate of hydrolysis of an ester is approximately proportional to the hydroxyl ion concentration, reactions of this type may also be used for investigating hydrolysis.§ The reaction velocity method is not applicable to the salt of a weak base and a weak acid, unless the dissociation constant of one of the components is known.

It should be emphasized that the method described can only be regarded as an approximate means for investigating the hydrolysis of salts, especially as it is the ions of weak acids and bases, which must be present in a hydrolysed salt solution, that have the largest catalytic influences. During the catalytic hydrolysis of an ester, free acid is being formed and the hydrogen ion concentration increases in the course of the reaction; on the other hand, saponification by hydroxyl ions results in the removal of the latter, so that in both cases the hydrolytic equilibrium, as well as the reaction velocity, will be affected. Corrections must therefore be made for such disturbing influences.||

Conductance Method—In a solution of 1 gm. equiv. of salt per litre, of which a fraction x is hydrolysed, there will be present $1 - x$ gm. equiv. of unhydrolysed salt, and x gm. equiv. of both free acid and base. If the base is very weak it may be regarded as completely un-ionized, and so it will contribute nothing towards the total conductance of the solution. The conducting power of

* Francis *et al.*, *ibid.*, 1912, 101, 2358; 1913, 103, 1722; 1915, 107, 1651; Brønsted and King, *J. Amer. Chem. Soc.*, 1925, 47, 2523. See also McBain and Bolam, *J. Chem. Soc.*, 1918, 113, 825.

† Osaka, *Z. physikal. Chem.*, 1900, 35, 702; Hudson, *J. Amer. Chem. Soc.*, 1907, 29, 1571; 1909, 31, 1136.

‡ Koelichen, *Z. physikal. Chem.*, 1900, 33, 149; Åkerlöf, *J. Amer. Chem. Soc.*, 1926, 48, 3046; 1927, 49, 2955; French, *ibid.*, 1929, 51, 3215.

§ Shields, *Z. physikal. Chem.*, 1893, 12, 167; *Phil. Mag.*, 1893, 35, 365; Hantzsch, *Ber.*, 1899, 32, 3066; Lundén, *loc. cit.*; Meyer, *Z. anorg. Chem.*, 1921, 115, 203.

|| See Shields, *loc. cit.*

1 gm. equiv. of a hydrolysable salt is thus made up of the conducting power of $1 - x$ gm. equiv. of unhydrolysed salt, and x gm. equiv. of free acid, i.e.

$$\Lambda = (1 - x)\Lambda_c + x\Lambda_{HA} \quad \dots \quad (\text{xlix})$$

where Λ is the apparent equivalent conductance of the solution (= the measured specific conductance \times vol. in c.c. containing 1 gm. equiv.), Λ_c is the equivalent conductance of the *unhydrolysed* salt at the particular dilution of the experiment, and Λ_{HA} is the equivalent conductance of the free acid. From this equation it follows that

$$x = \frac{\Lambda - \Lambda_c}{\Lambda_{HA} - \Lambda_c} \quad \dots \quad (1)$$

In order to determine x it is necessary to know Λ , Λ_c and Λ_{HA} ; of these Λ is obtained by direct measurement on the hydrolysed salt at the dilution studied. Λ_{HA} is generally taken as the equivalent conductance of the strong acid at infinite dilution, since its concentration is small; it is probably more accurate, however, to use the conductance of the acid at a concentration equivalent to that of the salt,* for the conductance of each constituent of a mixture depends on the total ionic concentration. Since the conductances of strong acids are well known, the appropriate value for Λ_{HA} can be readily found. The determination of Λ_c , however, presents a problem; Walker† used the following method of calculation. It had been found by Ostwald‡ that ions containing twelve or more atoms had a limiting mobility of about 35 units at 25° , hence Walker assumed this value for the anilinium ($C_6H_5 \cdot NH_3^+$) ion. The mobility of the chlorine ion was taken as 73, hence unhydrolysed aniline hydrochloride ($C_6H_5 \cdot NH_3 \cdot Cl$) should have an equivalent conductance at infinite dilution of 108 units; Λ_c could then be calculated by assuming an appropriate value for the conductance ratio at the particular dilution required. This method is, however, very approximate and of limited application.§ The most satisfactory determination of Λ_c can be made by using the principle suggested by Bredig;|| sufficient of the almost non-conducting free base is added to the salt solution until the hydrolysis is depressed nearly to zero. For example with aniline hydrochloride solution, free aniline is added until the conductance of the solution reaches a constant value; at this point hydrolysis is reduced to a negligible amount, and the conductance of the solution represents that of the

* Cf. Stieglitz and Derby, *Amer. Chem. J.*, 1904, 31, 449; see also p. 110 *supra*.

† *Z. physikal. Chem.*, 1889, 4, 333.

‡ *Ibid.*, 1888, 2, 840.

§ See also Ley, *loc. cit.*, for another approximate method.

|| *Z. physikal. Chem.*, 1894, 13, 213, 321.

un-hydrolysed salt, from which Λ_c can be calculated. Table XXIX contains some of Bredig's results with aniline hydrochloride; Λ_c^{64} and Λ_c^{32} are the equivalent conductances when the solution is $N/64$ and $N/32$, respectively, with respect to *added* free aniline.

TABLE XXIX

EQUIVALENT CONDUCTANCES OF ANILINE HYDROCHLORIDE SOLUTIONS AND DEGREES OF HYDROLYSIS

c	Λ	Λ_c^{64}	Λ_c^{32}	α	$k_h \times 10^5$
$N/64$	106.2	96.0	95.9	0.036	2.1
$N/128$	113.7	98.2	98.1	0.055	2.5
$N/256$	122.0	100.3	100.1	0.077	2.5
$N/512$	131.8	101.5	101.4	0.109	2.6
$N/1024$	144.0	103.3	103.3	0.147	2.5

Since the values of Λ_c^{32} are very little different from those of Λ_c^{64} , it is clear that even $N/64$ -aniline is sufficient to depress the hydrolysis of the salt almost to zero; the equivalent conductance of un-hydrolysed salt may, therefore, be regarded as equal to Λ_c^{32} in each case. The corresponding values of α have been calculated by means of equation (1), taking Λ_{HCl} as 380.*

For the salt of a strong base and a weak acid exactly the same method is applicable, except that the equation for the degree of hydrolysis reads :

$$\alpha = \frac{\Lambda - \Lambda_c}{\Lambda_{MOH} - \Lambda_c} \quad (1i)$$

The conductance method has also been used to study the hydrolysis of salts of weak acids and weak bases, although in such cases the calculation is somewhat more complicated.† An approximate treatment has been suggested by Arrhenius ‡ for aniline acetate. At a dilution of 50 litres per gm. equiv. the apparent equivalent conductance of this salt is 31.4 units; the value may be attributed, as a first approximation, to the un-hydrolysed aniline acetate, since the conductances of the free aniline and acetic acid may be neglected. The conductances of the anilinium and acetate ions may be taken as 35 and 43 respectively; hence Λ_0 for the salt should be 78 units at 25°. The conductance ratio at a dilution of 50–100 litres per gm. equiv. is probably about 0.9, and so the equivalent conductance at this dilution should be approximately 70. Since the apparent value is 31.4, the solution can only contain

* Strictly speaking Λ_{HCl} depends on the concentration of the salt, *vide supra*; in view of its magnitude compared with Λ_c , however, no serious error is involved in assuming a constant value.

† See Lundén, *J. Chim. phys.*, 1907, 5, 145; Kanolt, *J. Amer. Chem. Soc.*, 1907, 29, 1402; Noyes, Sosman and Kato, *ibid.*, 1910, 32, 159.

‡ *Z. physikal. Chem.*, 1890, 5, 16.

$31.4/70 = 0.45$ gm. equiv. of un-hydrolysed salt in 50 litres. The portion hydrolysed must, therefore, be about $1 - 0.45 = 0.55$, or 55 per cent. The concentration of free acetic acid can now be calculated roughly, and if an allowance is made for its conductance a more accurate value for the degree of hydrolysis of the salt may be calculated.

On the whole the conductance method for investigating hydrolysis is not regarded as accurate; * a great deal depends on a knowledge of the conductance of the un-hydrolysed salt, and the determination of this cannot be made with any degree of precision. The Bredig method is the most satisfactory, but it depends entirely on the added free acid or base having a negligible conductance; if this is not the case, it is sometimes possible to make an allowance for the error involved.†

Distribution Method—This was devised by Farmer ‡ and can be used if the weak constituent of the salt, but not the salt itself or the strong constituent, is soluble in a liquid immiscible with and insoluble in water. Consider the salt of a weak base; the latter is supposed to be soluble and have a normal molecular weight in benzene, say. If an aqueous solution of this salt is shaken with benzene the free base resulting from hydrolysis will distribute itself between the water and the benzene in a definite ratio, D .§ If the concentration in the benzene layer is determined by analysis, the concentration in the aqueous layer can be calculated and the hydrolytic constant can then be evaluated as follows. Suppose the concentration of salt is c gm. equiv. per litre, and that v_1 litres of this solution are shaken with v_2 litres of benzene until equilibrium is reached; the benzene layer is then found to contain m gm. equiv. of free base per litre. The concentration of free base in the aqueous layer at equilibrium must, therefore, be m/D gm. equiv. per litre. The amounts of free base in benzene and aqueous layers are mv_2 and mv_1/D gm. equiv. respectively; hence the amount of free acid in the v_1 litres of aqueous layer, assuming none has dissolved in the benzene, must be equal to the sum, i.e. $mv_2 + mv_1/D$ gm.

* See Farmer, *loc. cit.*, Lundén, *loc. cit.*

† See Noyes, Sosman and Kato, *loc. cit.* For applications of the conductance method, see also Salvadori, *Atti R. Accad. Lincei*, 1900, 9, (ii), 177; Zawidski, *Ber.*, 1903, 36, 3325; Stieglitz and Derby, *loc. cit.*; Kameyama, *Trans. Amer. Electrochem. Soc.*, 1921, 40, 131; Brady and Goldstein, *J. Chem. Soc.*, 1926, 1918; Gulezian and Müller (J. N.), *J. Amer. Chem. Soc.*, 1932, 54, 3151.

‡ *J. Chem. Soc.*, 1901, 79, 863; 1904, 85, 1713.

§ This distribution ratio, D , is equal to the concentration of base in the benzene layer, divided by the concentration in the aqueous layer; it can be determined by separate experiments with the base only. It is assumed that the value of D is not affected by the salt.

equiv. ; this must also represent the amount of salt hydrolysed in the volume v_1 . Since this volume contained originally cv_1 gm. equiv. of salt, the amount un-hydrolysed, when equilibrium with the benzene layer is attained, is $cv_1 - mv_2 - mv_1/D$ gm. equiv. It follows, therefore, that in the aqueous layer (vol. = v_1),

the concentration of free base is m/D gm. equiv. per litre,

„ „ „ „ acid is $\frac{mv_2}{v_1} + \frac{m}{D}$ gm. equiv. per litre,

„ „ „ un-hydrolysed salt is $c - \frac{mv_2}{v_1} - \frac{m}{D}$ gm. equiv. per litre.

If the un-hydrolysed salt and the free strong acid are assumed to be completely ionized, and the activity coefficients equal, and the weak base is regarded as completely un-ionized, the hydrolytic constant may be written :

$$k_h = \frac{\text{Conc. of free acid} \times \text{Conc. of free base}}{\text{Conc. of un-hydrolysed salt}} = \frac{\left(\frac{mv_2}{v_1} + \frac{m}{D}\right) \left(\frac{m}{D}\right)}{c - \frac{mv_2}{v_1} - \frac{m}{D}} \quad (\text{lii})$$

All the quantities required for the determination of k_h are thus known, and from a knowledge of k_h the degree of hydrolysis at any dilution may be calculated. The treatment for the salt of a weak acid and strong base is identical with that given here, except that a solvent for the acid is required. The distribution method for investigating hydrolysis can be applied to the study of a salt of two-sided weakness, provided a solvent can be found which dissolves either the acid or the base only.*

Freezing-Point Method—As a result of hydrolysis the number of osmotically active particles in the solution is increased above the normal value. If the solution contains c gm. equiv. of a salt MA per litre, and the degree of hydrolysis is α , there will be present at equilibrium :

$(1 - \alpha)c$ gm. equiv. of un-hydrolysed salt,

αc „ „ „ free strong base,

and αc „ „ „ free weak acid.

If i is the van 't Hoff factor (p. 16) for salt and base, whereas the un-ionized molecules of acid are assumed to follow the gas laws, the osmotic effect will be equivalent to $(ic + \alpha c)$ gm. mols. per

* For applications of the general method, see Farmer, *loc. cit.* ; Johnston, *loc. cit.* ; Szyszkowski, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1913, 2, No. 41 ; Westerberg, *Arkiv. Kim. Min. Geol.*, 1917, 6 ; Löfman, *Z. anorg. Chem.*, 1919, 107, 241 ; Williams (G.) and Soper, *J. Chem. Soc.*, 1930, 2469 ; for criticism, see McBain and Coleman, *ibid.*, 1914, 105, 1526.

litre. For a dilute solution i may be taken as 2, but alternatively the value may be obtained by comparison with a similar un-hydrolysed salt at the same total concentration. The depression of the freezing-point of water produced by 1 gm. mol. dissolved in a litre is roughly 1.86° , and so the hydrolysed salt solution should lower the freezing-point $c(i+x)1.86^\circ$. By actual measurement of the freezing-point lowering the value of x may be determined. This method is most useful when x is large, so that $(i+x)$ is appreciably different from i ; it has been applied by Walden,* and by Zawidski.†

In moderately concentrated solutions the osmotic effect is not strictly proportional to the molar concentration; hence an alternative method must be adopted in order to determine the value of the term $c(i+x)$. By experiments on a non-electrolyte of known molecular weight, e.g. cane sugar or fructose, a formula can be derived connecting the number of gm. mols. per litre with the depression of the freezing-point; if it is assumed that the same formula applies to the solution of hydrolysed salt the number of gm. mols., i.e. $c(i+x)$, per litre can be calculated and the value of x found. The method ‡ is applicable to salts of a weak base and weak acid, but the results are in any case only approximate. The osmotic activity of a solution is not merely a function of the number of gm. mols. per litre: it also depends on inter-ionic attractions (p. 144).

Vapour Pressure Method—This may be considered as a modification of the distribution method, in which a volatile acid, or base, is distributed between the aqueous solution and air. Since hydrocyanic acid is weak, a solution of an alkali cyanide contains a definite concentration of the un-ionized acid, and the latter has a definite partial vapour pressure. By comparison with the vapour pressures of hydrocyanic acid solutions of known concentration, the amount of free acid in the hydrolysed salt solution can be determined. In actual practice the vapour pressures are not measured directly. Air is bubbled at a definite rate through the alkali cyanide solution, and at exactly the same rate through hydrocyanic acid solutions; the free acid vaporizing with the air is then absorbed in a suitable reagent and the amounts compared in the two cases. The concentration of the solution of acid is altered until it vaporizes hydrogen cyanide at the same rate as does the hydrolysed salt solution; the concentration of free acid is then assumed to be the same in the two solutions. Actually it is the activities which are equal, but for a non-ionized molecule activity and concentration are almost identical unless the solution contains a large amount of other solutes;

* *Ber.*, 1901, 34, 4185.

† *Ibid.*, 1904, 37, 2289.

‡ See Goebel, *Z. physikal. Chem.*, 1914, 89, 49; Jellinek and Czerwinski, *ibid.*, 1922, 102, 438.

in any case the method is only approximate and it is superfluous, at this stage, to attempt a distinction between concentrations and activities. The concentration of free acid in the salt solution may be regarded as equal to x/c , and so the degree of hydrolysis x , and the hydrolytic constant may be determined.

This method* can, of course, only be used where the weak acid, or weak base, is appreciably volatile and the other constituent non-volatile; it has been applied in the study of ammonium salts, sodium phenoxide and alkali cyanides.

Dissociation Constant Method—The hydrolysis constant of a salt is related to the dissociation constant of the weak acid, or base, and the ionic product of water; thus k_h is equal to k_w/k_a , k_w/k_b , or $k_w/k_a k_b$, according as the acid, base or both are weak. The dissociation constants may be evaluated by conductance, or other measurements, and the ionic product can be determined by one of the methods described in the next section (p. 208); k_h may then be calculated and x evaluated at any particular dilution.

Electromotive Force Method—The hydrolytic constant may be determined if the hydrogen ion concentration of the salt solution is known (p. 201). Two methods involving (a) the hydrogen electrode and (b) the quinhydrone electrode, to be described later, are available for the accurate determination of hydrogen ion activities; the values so found may be substituted for the stoichiometrical concentrations in the approximate equations generally used. The hydrogen electrode cannot be used in solutions containing reducible ions or molecules, and the quinhydrone electrode is only applicable if pH is 8 or less. The hydrolysis of a number of salts has been investigated by these methods.†

Indicator Method—The hydrogen ion concentration of a salt solution may be determined approximately by means of indicators (see Chap. X), and from the result the hydrolytic constant may be evaluated.‡

Other Methods—A method depending on the solubility of

* Veley, *J. Chem. Soc.*, 1905, 87, 26; Hill, *ibid.*, 1906, 89, 1273; Naumann and Rücker, *J. prak. Chem.*, 1906, 74, 247; Naumann and Müller (W.), *ibid.*, p. 218; Worley and Browne, *J. Chem. Soc.*, 1917, 111, 1057; Harman and Worley, *Trans. Faraday Soc.*, 1925, 20, 502; Britton and Dodd, *J. Chem. Soc.*, 1931, 2332.

† Bjerrum, *Z. physikal. Chem.*, 1907, 59, 336; Denham, *J. Chem. Soc.*, 1908, 93, 41; Kablukoff and Sachanoff, *Z. physikal. Chem.*, 1909, 69, 419; Menzel, *ibid.*, 1922, 100, 276; Heyrovský, *J. Chem. Soc.*, 1920, 117, 11; Job, *Compt. rend.*, 1924, 179, 49, 1317; O'Sullivan, *Trans. Faraday Soc.*, 1925, 21, 319; Prytz, *ibid.*, 1928, 24, 281; Denham and Marris, *ibid.*, 1928, 24, 510, 515; Čupr., *Coll. Czech. Chem. Comm.*, 1929, 1, 377; *Z. anorg. Chem.*, 1931, 198, 310.

‡ Veley, *J. Chem. Soc.*, 1908, 93, 652, 2122; Tizard, *ibid.*, 1910, 97, 2490.

a salt of a weak acid and weak base, has been used by Löwenherz,* and one suggested by Denison and Steele involves the determination of ionic speeds.†

Review—Although the qualitative phenomena of hydrolysis have been definitely established, the experimental methods are not sufficiently exact for the quantitative determinations of degrees of hydrolysis and hydrolytic constants to be accurate. It is true that no attempt has yet been made to use activities in the determination of the constant, but in most methods other errors ‡ probably far outweigh that resulting from the application of ordinary concentration terms in the law of mass action. On the whole it may be concluded that the most accurate values for k_h can be obtained from a knowledge of k_a , or k_b , and k_w , since all the latter constants may be determined with a fair degree of accuracy.

Determination of the Ionic Product of Water.—The **Conductance Method**—Since water can act in an amphiprotic capacity, there must be an equilibrium between un-ionized molecules and hydrogen and hydroxyl ions (p. 188): it follows, therefore, that even the purest water should have a definite conducting power. This is in agreement with the fact that although the specific conductance of pure water is very small, repeated purification does not reduce the value below a fairly definite limit. After taking the greatest possible precautions to remove all impurities from the water, Kohlrausch and Heydweiller § obtained minimum values for the conductance at various temperatures; the specific conductances given in Table XXX have been calculated from these results.

TABLE XXX
SPECIFIC CONDUCTANCE (RECIP. OHMS $\times 10^{-6}$) OF PURE WATER

0°	18°	25°	34°	50°
0.015	0.043	0.062	0.095	0.187

It was first shown by Ostwald || that the ionic product could be calculated from the specific conductance of pure water, but his values were probably too high. Subsequently Kohlrausch and Heydweiller estimated that the specific conductance of perfectly pure water at 18° should be 0.0384×10^{-6} recip. ohms; this may be regarded as a measure of the conducting power of the ions in a 1 cm. cube of pure water. The ionic conductances at 18° of hydrogen and hydroxyl ions at very small concentrations are 315.2 and 173.8, respectively; therefore the conducting power of 1 gm. equiv. of

* *Z. physikal. Chem.*, 1898, 25, 385.

† *J. Chem. Soc.*, 1906, 89, 999.

‡ See Beveridge, *Proc. Roy. Soc. Edin.*, 1909, 29, 648; Harman and Worley, *loc. cit.*

§ *Z. physikal. Chem.*, 1894, 14, 317.

|| *Ibid.*, 1893, 11, 521.

H' and OH' ions is 489 recip. ohms. A cm. cube of pure water must then contain $0.0384 \times 10^{-6}/489$ gm. equiv. of H' and of OH' ions; hence 1 litre contains

$$\frac{0.0384 \times 10^{-6}}{489} \times 10^3 = 0.78 \times 10^{-7} \text{ gm. ions H' and OH'}$$

Since $[H'] = [OH'] = 0.78 \times 10^{-7}$,
 $k_w = [H'] [OH'] = 0.61 \times 10^{-14}$ at 18°

The conductivity method has also been used to determine the ionic products of ethyl alcohol*, formic acid,† acetic acid‡ and hydrogen chloride.§

Reaction Velocity Method—(a) The saponification of an ester is accelerated both by H' and OH' ions, and the velocity of the reaction is proportional to the separate concentrations of these ions, i.e.

$$\frac{dx}{dt} = k_1[H'] + k_2[OH'] \quad \text{. (liii)}$$

where k_1 and k_2 are the velocity constants for saponification by H' and OH', respectively, for a definite concentration of ester; these constants may be determined by direct experiments with acids and alkalis respectively. Wijs|| found that k_2/k_1 was about 1400 for methyl acetate at 25°; hence as long as the hydrogen ion concentration was low,

$$\frac{dx}{dt} \approx k_2[OH'] \quad \text{. (liv)}$$

Methyl acetate was hydrolysed with pure water and the reaction velocity in the early stages measured, at short intervals, by titrating the free acetic acid; the results were extrapolated to zero time so as to give the reaction velocity at the commencement of hydrolysis, i.e. by pure water. From the result, and a knowledge of k_2 , the value of $[OH']$ in pure water was determined as 0.1×10^{-7} gm. ions per litre at 25°. This method, owing to experimental difficulties, is only very approximate.

(b) Another method depending on the velocity of methyl acetate saponification was also used by Wijs.** In the reaction OH' ions are removed, but the H' ions which act catalytically increase in concentration, since $[H'] [OH']$ is constant. The result is that when pure water is the saponifying agent the reaction velocity first decreases as the hydroxyl ions are used up, reaches a minimum and then

* Danner and Hildebrand, *J. Amer. Chem. Soc.*, 1922, 44, 2824.

† Hammett and Dietz, *ibid.*, 1930, 52, 4795.

‡ Kolthoff and Willman, *ibid.*, 1934, 56, 1007.

§ Glockler and Peck, *J. Chem. Physics*, 1936, 4, 658.

|| *Z. physikal. Chem.*, 1893, 11, 492. ** *Ibid.*, 1893, 12, 514.

increases as the hydrogen ions accumulate. A formula was derived connecting the minimum velocity with the initial value in the presence of pure water, and from this $[\text{OH}']$, in pure water, could be determined as in the previous method. The minimum velocity of saponification of methyl acetate was obtained by measuring the rate of change of conductance of an ester-water mixture; the conductance was due almost entirely to the acetic acid resulting from decomposition of the ester, and so the rate of its increase was a measure of the reaction velocity. By this method the value of $[\text{OH}'] = [\text{H}']$, in pure water, was found to be 1.4×10^{-7} gm. ions per litre at 25° ; hence k_w is 1.96×10^{-14} .*

(c) The muta-rotation of glucose is catalysed both by hydrogen and by hydroxyl ions, and Hudson† found the velocity constant of the reaction could be expressed in the form:

$$k = 0.0096 + 0.258[\text{H}'] + 9750[\text{OH}'] \quad . \quad . \quad (lv)$$

For pure water, k was found to be 0.0106 at 24.7° , hence it follows that $[\text{H}'] = [\text{OH}'] = 1 \times 10^{-7}$ gm. ions per litre and k_w is 1×10^{-14} at 24.7° .

Salt Hydrolysis Method—The connection between k_w and k_h , the hydrolytic constant, has been discussed; if the latter is known, as well as the ionization constant of the acid, k_w may be determined. The method was first applied by Arrhenius‡ using the value of 0.008 per cent. as the degree of hydrolysis of 0.1 N-sodium acetate at 25° . In this case x is 0.00008, hence

$$k_h = \frac{x^2 c}{1 - x} = 0.64 \times 10^{-9}.$$

By separate measurements on the conductance of acetic acid it is known that k_a is 1.78×10^{-5} ; therefore,

$$\begin{aligned} k_w &= k_h k_a = 0.64 \times 10^{-9} \times 1.78 \times 10^{-5} \\ &= 1.14 \times 10^{-14} \text{ at } 25^\circ \end{aligned}$$

Several applications of the method have been made;§ Lundén studied the hydrolysis of *p*-nitrophenol and of 2:4:6-trimethylpyridine, and obtained a value for k_w of 1.05×10^{-14} at 25° ; as a result of measurements on the ammonium salt of diketotetrahydrothiazole, Kanolt concluded that k_w was 0.91×10^{-14} at 25° , whereas

* For an important modification of this method which does not need pure water, see Dawson, *J. Chem. Soc.*, 1927, 1146, 1290. The value obtained for k_w was 1.25×10^{-14} at 25° .

† *J. Amer. Chem. Soc.*, 1907, 29, 1571; 1909, 31, 1136.

‡ *Z. physikal. Chem.*, 1893, 11, 805.

§ Bredig, *ibid.*, p. 830; van Laar, *ibid.*, 1894, 12, 742; Lundén, *J. Chim. phys.*, 1907, 5, 574; Kanolt, *J. Amer. Chem. Soc.* 1907, 29, 1402; Noyes, Kato and Sosman, *ibid.*, 1910, 35, 159.

Noyes *et al.*, working with ammonium acetate, found k_w to be 0.82×10^{-14} at 25° .

Electromotive Force Methods—The details of this method will be described later; it depends on the determination of the *E.M.F.* of a cell consisting of hydrogen electrodes in acid and alkaline solutions (p. 387). The most accurate determinations indicate that the ionic product of water is $1.00 \pm 0.01 \times 10^{-14}$ at 25° .

A number of attempts have been made to determine the hydrogen ion concentration of pure water by *E.M.F.* methods, but only the most recent values, obtained by means of the glass electrode (p. 381) can be said to have any significance. According to Ellis and Kiehl,* the *pH* of pure water is 7.01 at 27.5° , so that k_w at this temperature is 0.98×10^{-14} ; this result, considering the great difficulty of measuring *E.M.F.*'s in a liquid of such high resistance and of preventing access of impurities, may be taken to be quite satisfactory. By means of specially adjusted indicator solutions the *pH* of pure water has been found to be 7.00 to 7.05 at 25° .†

Variation of k_w with Temperature—The value of k_w at different temperatures has been determined by various authors; reference has already been made to the work of Lundén, of Kanolt, and of Noyes and his collaborators; in addition computations have been made by Heydweiller,‡ based on the specific conductance of pure water and the ion conductances of H^+ and OH^- at various temperatures, and by Michaelis,§ Harned and Hamer,|| Wynne-Jones,** and Lorenz and Böhi,†† using *E.M.F.* methods. Some of the results are collected in Table XXXI.

TABLE XXXI
VALUES OF $k_w \times 10^{14}$ OBTAINED BY VARIOUS OBSERVERS

Temp.	Lundén.	Kanolt.	Heyd- weiller.	Lorenz and Böhi.	Noyes <i>et al.</i>	Harned and Hamer.
0°	—	0.30	0.12	0.14	0.09	0.11
10°	0.31	—	0.28	—	—	0.29
18°	—	0.68	0.59	0.72	0.46	—
25°	1.05	0.91	1.04	1.22	0.82	1.01
40°	—	—	—	—	—	2.92
50°	5.17	—	5.66	8.7	4.5	5.48
100°	—	—	58.2	74	48	—

Since the ionic product of water is proportional to the equilibrium constant of the reaction



* *Ibid.*, 1935, 57, 2145.

† Kolthoff and Kameda, *ibid.*, 1931, 53, 825.

‡ *Ann. Physik.* 1909, 28, 503.

§ *Hydrogen Ion Concentration*, Vol. I, Eng. trans., 1926, p. 25.

|| *J. Amer. Chem. Soc.*, 1933, 55, 2194.

** *Trans. Faraday Soc.*, 1936, 32, 1397.

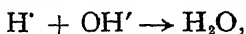
†† See p. 387.

and this constant increases with increasing temperature, it follows from Le Chatelier's principle that heat is absorbed in the ionization of water. Harned and Hamer have expressed the variation of k_w with temperature between 0° and 60° by means of the equation $\log k_w = -4787.3/T - 7.1321 \log T - 0.010365T + 22.801$ (lvi) where T is the absolute temperature. Applying the van 't Hoff isochore, it follows that

$$\Delta H = 21,926 - 14.812T - 0.04746T^2 \quad . \quad . \quad (lvii)$$

where ΔH , the increase in heat content, represents the heat absorbed, in calories, by the ionization of 1 gm. mol. of water. The values of the heat of ionization are thus $-14,513$, $-13,692$, $-13,481$ and $-11,936$ cal. at 0° , 20° , 25° and 60° , respectively.

It is well known that the neutralization of a strong acid with a strong base in dilute solution involves ultimately only the reaction:



i.e. the reverse of the ionization of water. The heat of neutralization in dilute solution should thus be numerically equal to the heat of ionization of water. The mean results obtained by Wörmann,* $14,710$ cal. at 0° and $13,410$ cal. at 25° , and by Richards and Rowe,† $13,693$ cal. at 20° , are in agreement with this view.

It will be seen from equation (lvii) that if the same relationship applies at high temperatures, the value of ΔH should decrease and eventually change sign as the temperature is raised: it follows, therefore, that the ionic product of water, which normally increases with temperature, should reach a maximum and then decrease. Noyes, and his collaborators,‡ found that k_w actually begins to decrease between 250° and 275° : this work was, however, carried out at high pressures and so the results may not fall into line with those obtained under ordinary atmospheric pressure.

Review—Although the different methods for the determination of k_w give results which are not in exact agreement, the similarity in the values is striking in view of the variety of methods used and of the small magnitude of the ionic product; the figures lend confirmation to the view that water is slightly ionized. It should be mentioned that in the majority of determinations k_w was measured in the presence of various salts, and the value in these circumstances is not necessarily the same as in pure water.

In the deduction of the equation $[H^+][OH^-] = \text{a constant } (k_w)$, it was assumed that the activity coefficients of the ions were unity,

* *Ann. Physik*, 1905, **18**, 793.

† Richards and Rowe, *J. Amer. Chem. Soc.*, 1922, **44**, 684; see also, Lambert and Gillespie, *ibid.*, 1931, **53**, 2632; Rossini, *Bur. Stand. J. Res.*, 1931, **6**, 847.

‡ *Loc. cit.*

and the activity of the water was constant. This is, no doubt, true in pure water or in very dilute solutions, but in more concentrated solutions the electrical environment causes appreciable changes in the activity coefficients of the ions; the presence of dissolved substances also lowers the vapour pressure, and the activity, of unionized water molecules. The value of k_w , as defined above, cannot therefore remain constant. Harned and his co-workers* have determined the value of the ionic product of water in a number of neutral halide solutions, by means of *E.M.F.* measurements; some examples of the effect of increasing concentration of salt on the ionization of water are shown in Fig. 12. In dilute solutions the ionic product is independent of the nature of the halide present, but in concentrated solutions the influence of the salt is specific. It

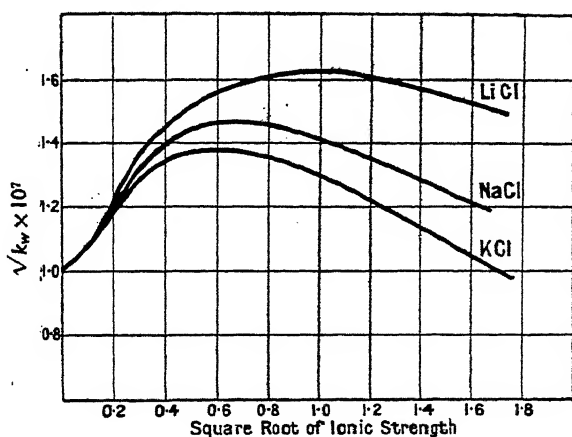


FIG. 12.—The ionic product of water in the presence of salts

must be realized that k_w , as ordinarily defined, is a constant for a definite environment only, and hence it is impossible to give it a definite value, except perhaps in pure water. For solutions up to 0.01*N* it is probable that the variation in k_w is not more than about 10 per cent., and for most purposes the values calculated by Heydweiller (Table XXXI) may be used without involving serious errors. Although k_w is a function of the ionic environment the quantity $a_{\text{H}^+} \times a_{\text{OH}^-}/a_{\text{H}_2\text{O}}$ must, by definition, always be constant at a given temperature; the activities of the ions and molecules concerned cannot be determined at all easily and so the constant

* See *Trans. Faraday Soc.*, 1927, 23, 462; *Trans. Amer. Electrochem. Soc.*, 1927, 51, 571, for earlier references; *J. Amer. Chem. Soc.*, 1930, 52, 3892; 1932, 54, 3112; 1933, 55, 2194, 2206, 2729, 4496, 4518; 1935, 57, 1873.

has little practical value. The ionic product k_w , therefore, although only approximately constant, is generally used.

The addition of an organic solvent, e.g. alcohol or acetone, alters the ionic product of water; * the former presumably alters the ionizing power of the medium.

Ionic Product of Heavy Water—The ionic product of deuterium oxide, that is $[D_2O'] [OD']$, has been measured by the *E.M.F.* method; † the values are less than those for ordinary water at the same temperatures. At 25° , for example, k_{D_2O} is 1.95×10^{-15} , compared with a k_{H_2O} value of 1.0×10^{-14} . The heat of ionization of deuterium oxide is apparently about 950 cal. greater, numerically, than for ordinary water; the heat of neutralization of a strong deuterio-acid by a deuterio-base should thus be approximately 14,650 cal. at 20° .

Other Ionic Products—As already mentioned (p. 209), the conductivity method has been applied to the determination of the ionic products of ethyl alcohol, of hydrogen chloride, and of acetic and formic acids. Many other solvents have a small but definite conductivity, ‡ but it is not always possible, e.g. with acetone, acetonitrile, nitrobenzene, to say what ions are responsible for the conducting power. In any case since these substances are not amphiprotic the ionic product, if any, can have little significance for the problems of lyolysis. Measurements of *E.M.F.* have been used to determine the ionic products of ethyl alcohol, § methyl alcohol || and of formic acid. **

* Löwenherz, *Z. physikal. Chem.*, 1896, **20**, 296; Pring, *Trans. Faraday Soc.*, 1921, **19**, 705; Lund, *J. Amer. Chem. Soc.*, 1927, **49**, 1346.

† Abel, Bratu and Redlich, *Z. physikal. Chem.*, 1935, **173**, 353; Wynne-Jones, *loc. cit.*

‡ For values see Kendall and Gross (P. M.), *J. Amer. Chem. Soc.*, 1921, **43**, 1426; Keyes *et al.*, *Trans. Amer. Electrochem. Soc.*, 1928, **54**, 127; Taylor, *Physical Chemistry*, 1931, Vol. I, p. 788 (Partington).

§ Danner and Hildebrand, *J. Amer. Chem. Soc.*, 1922, **44**, 2832.

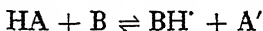
|| Buckley and Hartley (H.), *Phil. Mag.*, 1929, **8**, 320.

** Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 4239.

CHAPTER IX

NEUTRALIZATION AND BUFFER ACTION

NEUTRALIZATION of Acids and Bases—As seen in the previous chapter neutralization of an acid HA by a base B may be written in the most general sense as



in which the products BH' and A' are to be regarded as an acid and base respectively. If neutralization is to be appreciable it is clear (cf. p. 185) that the acid HA must be stronger than BH': that is to say, HA will lose a proton more readily than will BH'. The hydrogen ion activity of HA is, therefore, greater than that of BH' in the same solvent. It is evident that neutralization processes can be followed by studying changes of the appropriate hydrogen ion concentrations and this is the method generally adopted: it can be applied equally well to acids and bases of any type in solvents of all kinds, even those of an aprotic nature such as benzene. Since aqueous solutions are most frequently encountered the subject will be considered from the standpoint of water as solvent, but the treatment can be applied generally to all solvents, bearing in mind the limitations of each as regards proton accepting or donating power.

Strong Acid and Strong Base—The changes in hydrogen ion concentration occurring when a strong base is added gradually to a strong acid may be readily calculated, provided it may be assumed that the acid is completely ionized and the activity coefficient of the ions is unity. The hydrogen ion concentration at any stage is then equal to the amount of acid remaining un-neutralized. Suppose 100 c.c. of 0.1*N*-hydrochloric acid are titrated with 0.1*N*-sodium hydroxide; * then the values in Table XXXII may be calculated.

* In order to simplify the calculation it is assumed that the total volume remains constant at 100 c.c.; this assumption involves a slight error, but does not affect the main principles to be developed here. The value of k_w is taken as 10^{-14} , throughout

TABLE XXXII

NEUTRALIZATION OF 100 C.C. 0.1N-HCl by 0.1 N-NaOH
(VOLUME ASSUMED CONSTANT)

c.c. 0.1 N-NaOH added.	% HCl Un-neu- tralized.	[HCl] = [H] gm. equiv./litre.	pH
Nil	100.0	10^{-1}	1.0
50.0	50.0	5×10^{-2}	1.3
90.0	10.0	10^{-2}	2.0
99.0	1.0	10^{-3}	3.0
99.9	0.1	10^{-4}	4.0
100.0	Nil	—	7.0
100.1	Excess alkali	—	10.0

When 100 c.c. of alkali have been added the resulting solution is equivalent to one of sodium chloride, and since the latter is neutral the hydrogen ion concentration must be 10^{-7} gm. ions per litre, and the pH 7.0. If the addition of alkali is continued the solution will contain free alkali; on the assumption that this is completely ionized the value of $[\text{OH}']$, and hence of the pH, may be calculated. The total addition of 100.1 c.c. of alkali means that the free alkali concentration is 10^{-4} gm. equiv. per litre; hence $[\text{OH}']$ is 10^{-4} , $[\text{H}']$ must be 10^{-10} , and the pH of the solution is 10.0. These results indicate that in between the addition of 99.9 c.c. and 100.1 c.c. of alkali the pH of the solutions changes from 4 to 10; that is, in the vicinity of the equivalence point * the rate of change of pH of the solution is very rapid.

If the strong base is neutralized by the strong acid the variation of pH may be calculated in an exactly similar manner; the results in Table XXXIII are obtained in this way.

TABLE XXXIII

NEUTRALIZATION OF 100 C.C. 0.1N-NaOH BY 0.1 N-HCl
(VOLUME ASSUMED CONSTANT; $k_w = 10^{-14}$)

c.c. 0.1N-HCl added.	% NaOH Un-neu- tralized.	[NaOH] = $[\text{OH}']$.	pH
Nil	100.0	10^{-1}	13.0
50.0	50.0	5×10^{-2}	12.7
90.0	10.0	10^{-2}	12.0
99.0	1.0	10^{-3}	11.0
99.9	0.1	10^{-4}	10.0
100.0	Nil	—	7.0
100.1	Excess acid	—	4.0

The values given in Tables XXXII and XXXIII are plotted in Fig. 13, in which curve I shows the variation of pH with the degree

* This term is used throughout for the condition when the solution contains equivalent amounts of acid and alkali.

of neutralization of a strong acid and strong base ; * the two portions of the curve may be regarded as parts of one continuous curve representing the change of hydrogen ion concentration as a strong acid is titrated with a strong base until the solution contains a large excess of the latter, or vice versa. The form of the neutralization curve depends on the concentration of the solution, and curve II is that for $10^{-4}N$ -solutions of strong acid and alkali ; it

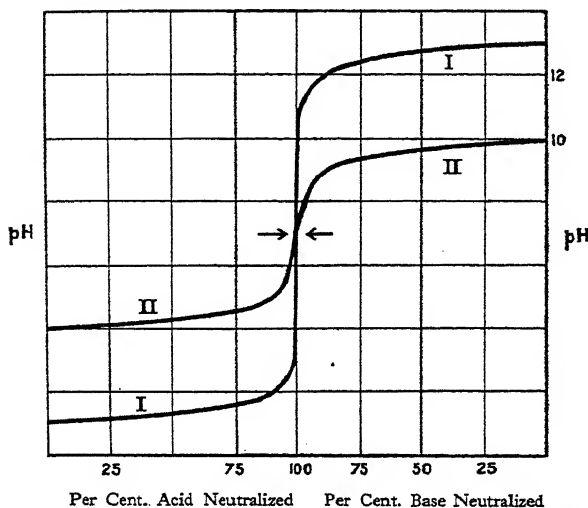


FIG. 13.—The neutralization curves of strong acid and strong base

is important to note that the change of pH at the equivalence point is less marked the more dilute the solutions.

Strong Acid and Weak Base—At the equivalence point, in such a case, the pH is not 7.0, since the solution is hydrolysed and reacts acid ; the actual pH can be determined by the use of equation (xxxii), page 195, the dissociation constant of the base being known. Before the equivalence point is reached, however, the excess of acid represses hydrolysis, and the course of neutralization is the same as for a strong base. The left hand side of the pH -neutralization curve is, except for the equivalence point, as in Fig. 13 ; the nature of the other half of the curve will be discussed later.

Weak Acid and Strong Base—The calculation is somewhat more complicated because (i) the acid is only slightly ionized ; (ii) the salt formed represses this ionization ; and (iii) the salt is hydrolysed. The following method may be used. Let a represent

* For the importance of pH -neutralization curves considered in this chapter for analytical work, see pp. 260, 390 *infra* ; also, see Kolthoff and Furman, *Indicators* ; Smith (T. B.), *Analytical Processes*, 1929, p. 153 *et seq.*

the total initial concentration of weak acid HA ; during neutralization by a strong base MOH this is converted into a salt MA, assumed to be completely ionized into M' and A' ions. If b is the concentration of the base added at any instant, then $[M']$ is equal to b , since the base, like the salt, is completely ionized. As the acid HA is only partially neutralized, at any instant

$$a = [HA] + [A'] \quad \dots \quad (i)$$

Further, as the solution must be electrically neutral the sum of all the positive charges must be equal to the sum of the negative charges, i.e.

$$[M'] + [H'] = [A'] + [OH'] \quad \dots \quad (ii)$$

or

$$b + [H'] = [A'] + [OH'] \quad \dots \quad (iii)$$

By means of these equations the terms $[A']$ and $[HA]$ may be eliminated from the expression for the *true* ionization constant of the acid :

$$K_a = \frac{[H'] [A'] f_H f_{A'}}{[HA] f_{HA}}$$

If the activity coefficient of the un-ionized acid is taken as unity, then it is found that

$$f_H [H'] = K_a \frac{a - b - [H'] + [OH']}{f_{A'} (b + [H'] - [OH'])} \quad \dots \quad (iv)$$

The term $[OH']$ may be replaced by $k_w/[H']$ but the equation then becomes a cubic involving $[H']^3$, $[H']^2$, etc., and a solution is difficult ; some simplification is therefore made before proceeding. As long as the solution is acid, $[OH']$ is small and may be neglected ; the equation reduces to

$$f_H [H'] = K_a \frac{a - b - [H']}{f_{A'} (b + [H'])} \quad \dots \quad (v)$$

This form is essential if the solution is acid, and not too concentrated, but if the concentration of base added, i.e. the term b , is appreciable, the quantity $[H']$ may be neglected in comparison with it, and the equation becomes

$$f_H [H'] = K_a \frac{a - b}{f_{A'} b} \quad \dots \quad (vi)$$

Since a is the original concentration of acid, and b the concentration of added base, $a - b$ represents the concentration of un-neutralized acid, and b the concentration of salt formed, therefore

$$f_H [H'] = K_a \frac{[\text{Un-neutralized Acid}]}{f_{A'} [\text{Salt}]} \quad \dots \quad (vii)$$

or

$$pH = pK_a + \log [\text{salt}]/[\text{acid}] + \log f_{A'} \quad \dots \quad (viii)$$

As the activity coefficient of the A' ions cannot be determined

readily—although an approximate estimate may be made from the Debye-Hückel theory*—it is generally assumed to be equal to unity, and K_a is replaced by the classical constant k_a ; it is to be noted that pH may be assumed to include the activity coefficient, f_{H^+} , of the hydrogen ions (p. 189, footnote). The equation for pH then becomes

$$pH = pk_a + \log [\text{salt}]/[\text{acid}] \quad \text{. (ix)}$$

This equation is generally known as the Henderson-Hasselbalch,† or more simply, the Henderson, equation;‡ it holds quite well between pH 4 and pH 10 for solutions which are not too dilute.

By means of the simplified Henderson equation the pH during the neutralization of a weak acid with a strong base, except at the beginning and end of the process, may be calculated. For these extreme cases the general equation (iv) is still applicable, suitable approximations being made to simplify the calculation. When the weak acid only is present b is zero, $[OH']$ may be neglected, and f_{H^+} and $f_{A'}$ may both be taken as unity; hence

$$[H^+] = k_a \frac{a - [H^+]}{[H^+]} \quad \text{. (x)}$$

$$\text{and} \quad [H^+] = -\frac{k_a}{2} + \sqrt{\frac{k_a^2}{4} + ak_a} \quad \text{(xi)}$$

$$\text{If } [H^+] \text{ or } k_a \text{ is small, } [H^+] = \sqrt{ak_a} \quad \text{. (xii)}$$

Both these equations may be derived directly from the Ostwald equation (p. 95); they enable the hydrogen ion concentration of the acid solution at the commencement of titration to be calculated.

At the end of the 'neutralization', or more exactly, at the equivalence point, a and b are equal, and $[H^+]$ may be neglected, since the solution is alkaline owing to hydrolysis; taking activity coefficients as unity, equation (iv) then reduces to

$$[H^+] = k_a \frac{[OH']}{a - [OH']} \quad \text{. (xiii)}$$

If the solution is not too dilute $[OH']$ may be neglected in comparison with a , and $[OH']$ in the numerator may be replaced by $k_w/[H^+]$; then

$$[H^+] = \sqrt{k_w k_a / a} \quad \text{. (xiv)}$$

* See p. 241 for this development.

† Henderson, *J. Amer. Chem. Soc.*, 1908, 30, 954; Hasselbalch, *Biochem. Z.*, 1917, 78, 112, first used the exponential form.

‡ This approximate equation may be obtained by another method. In general $f_{H^+}[H^+] = K_a[HA]/[A']f_{A'}$; if the free acid present is completely un-ionized, and the salt MA completely ionized, $[HA] = [\text{un-neutralized acid}]$, and $[A'] = [\text{salt}]$; hence $f_{H^+}[H^+] = K_a [\text{un-neutralized acid}]/f_{A'} [\text{salt}]$, or, approximately, $pH = pk_a + \log [\text{salt}]/[\text{acid}]$.

which is identical, as it should be, with equation xxvi (p. 193) for the hydrogen ion concentration of a hydrolysed solution of the salt of a weak acid and strong base.

It is thus possible to calculate, with reasonable accuracy, the whole of the pH -neutralization curve; for a definite instance, e.g. the titration of 100 c.c. of 0.1*N*-acetic acid, for which k_a is 1.8×10^{-5} , with 0.1*N*-sodium hydroxide, the values given in Table XXXIV may be calculated.

TABLE XXXIV
NEUTRALIZATION OF 100 C.C. 0.1*N*-ACETIC ACID BY 0.1*N*-NaOH
(VOLUME ASSUMED CONSTANT)

c.c. 0.1 <i>N</i> -NaOH added.	% 0.1 <i>N</i> - Acetic Acid Un- neutralized.	[Acid].	[Salt].	[H ⁺].	pH
Nil	100.0	0.1		1.34×10^{-3}	2.87
10.0	90.0	0.09	0.01	1.62×10^{-4}	3.79
20.0	80.0	0.08	0.02	7.2×10^{-5}	4.14
40.0	60.0	0.06	0.04	2.7×10^{-5}	4.57
50.0	50.0	0.05	0.05	1.8×10^{-5}	4.74
70.0	30.0	0.03	0.07	7.7×10^{-6}	5.11
90.0	10.0	0.01	0.09	2.0×10^{-6}	5.70
99.0	1.0	0.001	0.099	1.8×10^{-6}	6.74
99.9	0.1	0.0001	0.0999	1.8×10^{-6}	7.74
100.0	Nil		0.10	1.34×10^{-6}	8.87

The variation of pH during the neutralization of a strong base by means of a weak acid is almost identical with that for a strong acid (Table XXXII), except in the very close vicinity of the equivalence point when the hydrolysis of the salt, hitherto repressed by excess of free base, is appreciable. If the weak acid is acetic acid, for example, the pH at the equivalence point, as shown in Table XXXIV for the reverse titration, is 8.87 for 0.1*N*-solutions. The complete curve for the neutralization of 0.1*N*-acetic acid by 0.1*N*-sodium hydroxide, and vice versa, is given in Fig. 14 (I); the right-hand side being, of course, almost identical with that of curve I in Fig. 13. The sudden change of pH at the equivalence point is less marked than for a strong acid; it occurs roughly between pH 8 for 0.1 per cent. excess acid and pH 10, for 0.1 per cent. excess alkali. It is interesting to note that when the acid is 50 per cent. neutralized, $[salt] = [acid]$, and $[H^+]$ is equal to k_a ; by measuring the pH of the solution a method is available for the determination of the dissociation constant of the acid.

If a more dilute solution of acetic acid, e.g. 0.01*N*, is titrated with a strong alkali the nature and position of the curve is not seriously affected; the pH at the commencement of neutralization is 3.37, and at the equivalence point it is 8.37 instead of 2.87 and 8.87 respectively, for 0.1*N*-acid. In the intermediate stages the

pH 's calculated from the Henderson equation are independent of dilution; hence the pH -neutralization curve is almost identical with that in Fig. 14 (I).

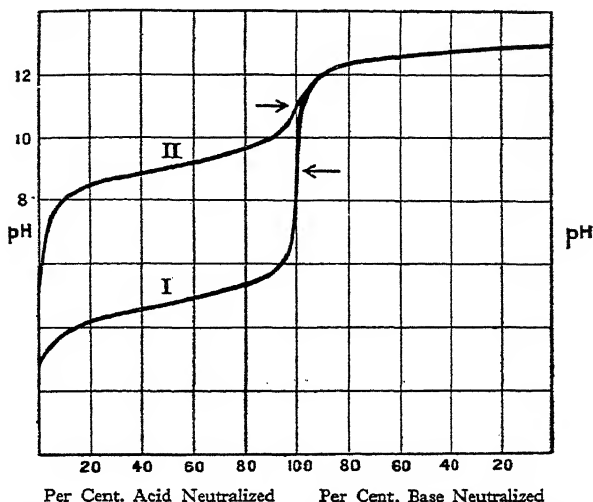


FIG. 14.—The neutralization curves of weak acids (I and II) and a strong base

When the acid is moderately strong the pH may be less than 4 for an appreciable part of the early stages of neutralization: it is then not justifiable to neglect the quantity $[H']$ in the numerator and denominator of equation (v). The latter then reduces to

$pH = pK_a + \log ([\text{salt}] + [H']) / ([\text{acid}] - [H']) + \log f_A$. (xv)
or, solving for $[H']$, it takes the form

$$[H'] = \frac{1}{2}[(a - b) + \sqrt{(a - b)^2 - 4(b + k_a)}] \quad . \quad (xva)$$

activity coefficients being ignored.

For a very dilute solution ($< 0.001N$) of an acid of k_a about 10^{-5} , or for more concentrated solutions ($0.01N$) of weaker acids ($k_a < 10^{-7}$), the hydrolysis of the salt, which is assumed in the simple Henderson equation to be repressed, is appreciable at a comparatively early stage of neutralization. Since the hydrogen ion concentration in these solutions is small right from the commencement, it is not justifiable to neglect $[OH']$ in comparison with $[H']$; in fact if the pH is greater than 10, it is more accurate to neglect $[H']$ and retain $[OH']$. The general equation (iv), page 218, which is applicable under *all* circumstances, may then be reduced to the form

$$[H'] = k_a \frac{a - b + [OH']}{b - [OH']} \quad . \quad . \quad . \quad (xvi)$$

if the activity coefficients are assumed to be equal to unity. For $[\text{OH}']$ may be substituted $k_w/[\text{H}']$, hence

$$[\text{H}'] = k_a \frac{a - b + k_w/[\text{H}']}{b - k_w/[\text{H}']} \quad (\text{xvii})$$

or $b[\text{H}']^2 + [\text{H}'](bk_a - ak_a - k_w) - k_wk_a = 0$.

Neglecting k_w in comparison with $(bk_a - ak_a)$ —the error is small even at the equivalence point since $[\text{H}']$ is so small—the equation may be solved for $[\text{H}']$, thus:

$$[\text{H}'] = \frac{k_a}{2b} \left[(a - b) + \sqrt{(a - b)^2 + 4bk_w/k_a} \right] \quad (\text{xviii})$$

The hydrogen ion concentration at the equivalence point, when $a = b$, is found, as previously, to be equal to $\sqrt{k_wk_a/a}$.

The $p\text{H}$'s calculated from equation (xviii) for various stages of the neutralization of a 0.1*N*-solution of an acid of $k_a = 10^{-9}$ are given in Table XXXV; up to $p\text{H}$ 10 the Henderson equation may be used without causing any appreciable error, but beyond this point the more accurate equation must be applied.

TABLE XXXV

NEUTRALIZATION OF 100 C.C. 0.1*N*-ACID $k_a = 10^{-9}$ BY 0.1*N*- NaOH
(VOLUME ASSUMED CONSTANT)

c.c. 0.1 <i>N</i> - NaOH added.	% 0.1 <i>N</i> -acid Neutralized.	$[\text{H}']$.	$p\text{H}$.
Nil	Nil	10^{-5}	5.00
5.0	5.0	1.9×10^{-6}	7.72
10.0	10.0	9×10^{-7}	8.05
30.0	30.0	2.33×10^{-8}	8.63
50.0	50.0	10^{-9}	9.00
70.0	70.0	4.3×10^{-10}	9.37
90.0	90.0	1.1×10^{-10}	9.96
95.0	95.0	5.2×10^{-10}	10.28
99.0	99.0	1.62×10^{-11}	10.79
99.5	99.5	1.28×10^{-11}	10.89
99.9	99.9	1.05×10^{-11}	10.98
100.0	100	10^{-11}	11.00

These results are shown graphically by curve II in Fig. 14; the alkaline side of the curve is almost the same as in previous cases, except in the vicinity of the equivalence point. In this region equation (iv), being quite general, is still applicable.

For a very weak acid the $p\text{H}$ change is gradual over the whole of the neutralization range; the $p\text{H}$ in the instance considered here changes from $p\text{H}$ 10.98 at 0.1 per cent. excess acid to $p\text{H}$ 11.02 at 0.1 per cent. alkali. For dilute solutions the inflexion in the $p\text{H}$ -neutralization curve is always less marked than in the more

concentrated solutions: if ak_a is less than $27k_w$ no inflexion can be detected.*

Weak Base and Strong Acid—Using the methods applied in the case of a weak acid and strong base there may be deduced (a) the general equation, applicable in all circumstances:

$$f_{\text{OH}'}[\text{OH}'] = K_b \frac{b - a - [\text{OH}'] + [\text{H}']}{f_{\text{M}}(a + [\text{OH}'] - [\text{H}'])} \quad (\text{xix})$$

where b is the concentration of the solution of base, and a is the acid added, (b) the form used when $[\text{H}']$ is small, i.e. when $p\text{H} > 10$,

$$f_{\text{OH}'}[\text{OH}'] = K_b \frac{b - a - [\text{OH}']}{f_{\text{M}}(a + [\text{OH}'])} \quad (\text{xx})$$

(c) the form when $[\text{OH}']$ is small, i.e. when $p\text{H} < 4$, applicable during the neutralization of a very weak base, or a very dilute solution of a base of medium weakness,

$$f_{\text{OH}'}[\text{OH}'] = K_b \frac{b - a + [\text{H}']}{f_{\text{M}}(a - [\text{H}'])} \quad (\text{xxi})$$

and (d) the simple equation which is sufficiently accurate between $p\text{H} 4$ and $p\text{H} 10$:

$$f_{\text{OH}'}[\text{OH}'] = K_b \frac{b - a}{f_{\text{M}} \cdot a} \quad (\text{xxii})$$

or $p\text{OH} = pK_b + \log [\text{salt}]/[\text{base}] + \log f_{\text{M}} \quad (\text{xxiii})$

In every case for ease of calculation the activity coefficients may be taken as unity, and in the simple equation this yields

$$p\text{OH} = pK_b + \log [\text{salt}]/[\text{base}] \quad (\text{xxiv})$$

or $p\text{H} = pK_w - pK_b - \log [\text{salt}]/[\text{base}] \quad (\text{xxv})$

The $p\text{H}$ -neutralization curves for bases of various ionization constants, and for solutions of different concentrations are exactly analogous to those for weak acids, except that the former appear, of course, at the top right-hand portion of the $p\text{H}$ -neutralization diagrams. The weaker the base, and the less concentrated the solution, the smaller the inflexion in the vicinity of the equivalence point, as in the neutralization of weak acids. The $p\text{H}$ at the equivalence point may be obtained in a manner analogous to that used above, or else equation (xxxiii) of the previous chapter (p. 195) can be utilized.

Weak Acid and Weak Base†—Since the base is weak the

* See Eastman, *J. Amer. Chem. Soc.*, 1925, 47, 333; Roller, *ibid.*, 1928, 50, 1; see also p. 390 *infra*.

† For the following treatment, which is more satisfactory than that given in the earlier edition, the author is indebted to Dr. T. B. Smith. Activity coefficients are omitted for simplicity, and also an account of other approximations that have to be made.

salt formed will be appreciably hydrolysed, and the simple formulæ are no longer applicable unless acid or base is present in fair excess. Further, b is no longer equal to $[M']$, but

$$b = [M'] + [MOH] \quad \dots \quad (xxvi)$$

$$\text{and} \quad a = [A'] + [HA] \quad \dots \quad (xxvii)$$

Since the solution must be electrically neutral,

$$[M'] + [H'] = [A'] + [OH'],$$

and a combination of this equation with those for a and b gives

$$[HA] - [BOH] = a - b + [OH'] - [H'] \quad (xxviii)$$

Substituting for $[A']$ the value given by equation (xxvii) in the ordinary equation for the dissociation constant of the weak acid, thus

$$k_a = \frac{[H'] [A']}{[HA]} = \frac{[H'](a - [HA])}{[HA]}$$

$$\therefore [HA] = a[H']/(k_a + [H']).$$

In an exactly similar manner, using the relationship for k_b , it follows that

$$[BOH] = b[OH']/(k_b + [OH']).$$

Inserting these values for $[HA]$ and $[BOH]$ in equation (xxviii), there results

$$\frac{a[H']}{k_a + [H']} - \frac{b[OH']}{k_b + [OH']} = a - b + [OH'] - [H'] \quad (xxix)$$

This equation, apart from the omission of activity coefficients, is exact, but when $[OH']$ is replaced by $k_w/[H']$ it is seen to be of the fourth order. If it is to be solved easily, therefore, approximations have to be made. In the first stages of neutralization, the extent of hydrolysis is small and so the second term on the left-hand side, giving the value of $[BOH]$ can be neglected. For a moderately strong acid $[OH']$ can also be ignored, and the resulting quadratic equation gives the same solution for $[H']$ as is obtained from equation (xv). If the acid is weak then in the very early stages both $[OH']$ and $[H']$ may be neglected, in addition to the $[BOH]$ term, and the result is equivalent to the simple Henderson equation. For the later parts of the neutralization range, however, $[BOH]$ must be included, and a reasonably justifiable simplification is to assume that $[OH'] - [H']$ is negligible; the resulting quadratic when solved gives

$$[H'] = \frac{k_a}{2b} \left[(a - b) + \sqrt{(a - b)^2 + 4a^2k_w/k_ak_b} \right] \quad (xxx)$$

From these relationships the values of $[H']$ at various stages of neutralization of a weak acid by a weak base can be determined.

The results in Table XXXVI have been calculated for the neutralization of 0.1*N*-acetic acid ($k_a = 1.8 \times 10^{-5}$) by 0.1*N*-ammonium hydroxide (k_b assumed 1.8×10^{-5}). The value of $[H^+]$ at the equivalence point is calculated from equation (xliii), p. 197,

$$[H^+] = \sqrt{k_w k_a / k_b}$$

for the salt of a weak acid and weak base; as is to be expected, equation (xxix), above, reduces to this form when $a = b$.

TABLE XXXVI
NEUTRALIZATION OF 100 C.C 0.1*N*-ACETIC ACID BY 0.1*N*-NH₄OH
(VOLUME ASSUMED CONSTANT)

c.c. 0.1 <i>N</i> -NH ₄ OH added.	% Acetic Acid Neutralized.	$[H^+]$.	pH.
Nil	Nil	1.34×10^{-7}	2.87
10	10	1.62×10^{-7}	3.79
50	50	1.8×10^{-7}	4.74
90	90	2.0×10^{-7}	5.70
95	95	9.6×10^{-8}	6.02
98	98	3.9×10^{-8}	6.41
99	99	2.25×10^{-8}	6.65
99.5	99.5	1.54×10^{-8}	6.81
100	100	1.34×10^{-7}	7.0

If a weak base is titrated with a weak acid the exact equation (xxviii), applicable over the whole acid-base range, may be simplified by neglecting the first term on the left-hand side and $[H^+]$ in the early stages of the titration. Later, however, the $[HA]$ term must be included, but $[OH^-] - [H^+]$ can be ignored: this gives the same result as equation (xxix), which can thus be used for stages of appreciable neutralization in either direction. For the addition of acid to base, b is the initial concentration of the base and a represents the amount of acid added at any instant. The calculations have been made for the neutralization of 0.1*N*-ammonium hydroxide with 0.1*N*-acetic acid, the reverse of the previous case, and the results are given in Table XXXVII* (p. 226).

The results quoted in Tables XXXVI and XXXVII are plotted in Fig. 15; it is seen that although the equivalence point corresponds to neutrality, pH 7,† the change of pH in this vicinity, and

* It is of interest to note that the simple Henderson equations give results almost identical with those quoted in Tables XXXVI and XXXVII up to 90 per cent. neutralization in either direction; beyond this point hydrolysis becomes appreciable and the $[HA]$ or $[BOH]$ terms cannot be neglected.

† This is not exactly true, but it appears so since k_a and k_b have been assumed equal to simplify the calculation; the actual difference is very small.

TABLE XXXVII

NEUTRALIZATION OF 100 C.C. 0.1*N*-NH₄OH BY 0.1*N*-ACETIC ACID
(VOLUME ASSUMED CONSTANT)

c.c. 0.1 <i>N</i> -Acetic Acid added.	% NH ₄ OH Neutralized.	[H ⁺].	pH.
0	Nil	7.5×10^{-12}	11.13
10	10	6.2×10^{-11}	10.21
50	50	5.5×10^{-10}	9.26
90	90	5.0×10^{-9}	8.30
95	95	1.04×10^{-8}	7.98
98	98	2.56×10^{-8}	7.59
99	99	4.43×10^{-8}	7.35
99.5	99.5	6.48×10^{-8}	7.19
100	100	10^{-7}	7.0

in fact during the whole of the neutralization, is very gradual. If the solutions are more dilute, or the dissociation constants smaller, the inflexion is even less marked.

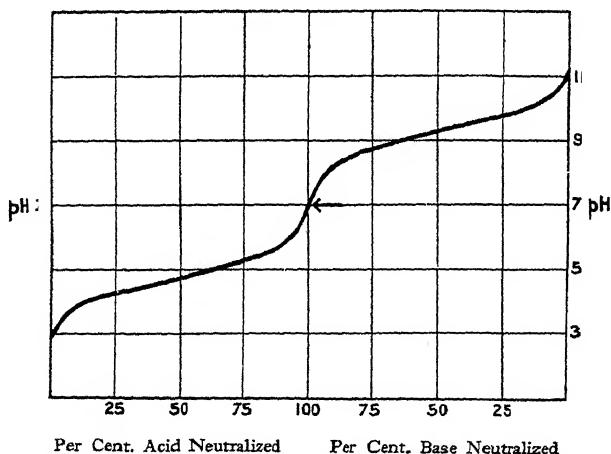


FIG. 15.—The neutralization curve of ammonia and acetic acid

Neutralization in Non-Aqueous Media—When a strong acid is added to the alkali salt of a weak one, in a so-called displacement reaction, the pH curve must have the same shape as that for the neutralization of the weak acid itself by a strong base,* as shown in Fig. 14, except that it starts from the centre, which represents

* If to 1 equiv. of weak acid HA there is added x equiv. of NaOH, the solution contains $1 - x$ equiv. of HA and x equiv. of NaA; the same ratio is obtained by adding $1 - x$ equiv. of HCl to 1 equiv. of NaA. Since the pH depends on the ratio of weak acid to salt (Henderson equation) it will be the same in both cases.

the salt, and finishes at the left-hand side, that is at the free acid. For an acid such as acetic, the curve will resemble Fig. 14 (I), and it is evident that there will be no sharp inflexion at the equivalence point; for the salt of a very weak acid, however, see Fig. 14 (II), the break will be appreciable. The same conclusions can be reached in a more fundamental manner from the modern view of acids and bases. A displacement reaction can be regarded as a neutralization (p. 184), and it will be accompanied by a change of hydrogen ion activity just as in a conventional neutralization process. The reaction between sodium acetate and a strong acid is equivalent to the 'neutralization' of the acetate ion base by the acid. In general, the dissociation constant of a base is equal to K_I/K_A (see p. 186), where K_I is the ionic product of the solvent and K_A the dissociation constant of the conjugate acid: in the case under discussion this becomes k_w/k_a , where k_a is the dissociation constant of acetic acid,* and so is about 5.5×10^{-10} . The acetate ion is thus an extremely weak base, and the slight inflexion at the equivalence point is understood. The same argument applies to the ammonium ion, which has an acid dissociation constant of approximately 5×10^{-10} , when 'neutralized' by a strong alkali. It follows, therefore, that only with salts of very weak acids or bases, so that the conjugate base or acid, respectively, has a relatively large dissociation constant, is there any considerable inflexion in the pH curve at the completion of the displacement reaction.

In order to increase the inflexion, a condition highly desirable for analytical purposes (see pp. 260, 390), special procedures may be adopted involving the use of non-aqueous solvents. It will be evident from the discussion in the previous sections that the inflexion in the pH-neutralization curve in the vicinity of the equivalence point is greater the smaller the extent of hydrolysis, that is to say the smaller the quantity k_w/k , the hydrolysis constant, where k is the dissociation constant of the weak acid or weak base being neutralized. If it were possible to decrease k_w considerably without affecting k very greatly, the hydrolysis would be diminished and the inflexion more marked: for acids and bases consisting of cations, e.g. NH_4^+ , or anions, e.g. CH_3CO_2^- , respectively, the dissociation constant in ethyl alcohol is only slightly less than in water,†

* It will be observed that the dissociation constant of an anion base is equal to the hydrolysis constant of the salt of the weak acid: an analogous relationship holds for cation acids (cf. p. 183).

† The dissociation of an uncharged acid, e.g. acetic, or base, e.g. ammonia, involves the formation of positive and negative ions from a neutral molecule, and so it is to be expected that if the dielectric constant of the medium is diminished, e.g. replacing water by ethyl alcohol, the dissociation constant should be decreased, since the electrostatic forces between the ions are increased. For a charged acid, e.g. NH_4^+ , or base, e.g. CH_3CO_2^- ,

but the ionic product is diminished nearly a million fold. It is clear that lyolysis, using the term in its widest sense, during the 'neutralization' of acetate by a strong acid, or of an ammonium salt by a strong base, will be much less in ethyl alcohol than in water and so a sharper inflexion will occur in the pH curve. The same arguments apply to substituted ammonium ions, for example such as exist in the salts of amines and of amino-acids.* The inflexion is found to be most marked in the absence of water.

Another method for suppressing lyolysis in the neutralization of any weak base, whether of the charged or uncharged type, is to utilize the relationship deduced on p. 185, and to employ a strongly protogenic medium, e.g. acetic or formic acid. It has been found experimentally that in such solvents weak bases of the anion type, e.g. acetate and formate, as well as those of the conventional type, e.g. amines, amides, etc., give pH -neutralization curves with sharp inflexions at the equivalence points.† Similar results have been obtained in the neutralization of the basic portions of amino-acids dissolved in pure acetic acid.‡ For an appreciable inflexion of pH in the neutralization of a weak acid it would be necessary to employ a strongly basic solvent, e.g. liquid ammonia, or one which is protophilic only, e.g. ether or acetonitrile. As a general rule there will be no appreciable inflexion in the pH -neutralization curve for a weak acid and a weak base, no matter what the medium, except possibly for a suitable acid-base system in an aprotic solvent.§

Neutralization of a Mixture of Two Monobasic Acids—

The variation of pH during the neutralization of a mixture of acids in aqueous solution may be calculated in the following manner. Let a_I and a_{II} be the initial concentrations of the two acids HA_I and HA_{II} , their dissociation constants being k_I and k_{II} respectively; suppose that at a certain stage of the neutralization a concentration b

on the other hand, there is no such separation of ions and the effect of changing the medium on the dissociation constant would be relatively small (cf. Brønsted, *Chem. Reviews*, 1928, 5, 231). The dissociation constant of an uncharged acid generally changes by a factor of 10^{-6} , and of an uncharged amine base by a factor of about 10^{-4} , in passing from water to ethyl alcohol (see Kolthoff, *J. Physical Chem.*, 1931, 35, 2732; Goodhue and Hixon, *J. Amer. Chem. Soc.*, 1934, 56, 1329).

* Bishop, Kittredge and Hildebrand, *ibid.*, 1922, 44, 135; Kolthoff, *loc. cit.*; Neuberger, *Proc. Roy. Soc.*, 1934, 115 B, 180; Ogston and Brown (J. F.), *Trans. Faraday Soc.*, 1935, 31, 574.

† Hall (N. F.) and Conant, *J. Amer. Chem. Soc.*, 1927, 49, 3047; Hall and Werner, *ibid.*, 1928, 50, 2367; Hammett and Dietz, *ibid.*, 1930, 52, 4795. For theory of titration in acetic acid, see Kilpi, *Z. physikal. Chem.*, 1936, 177, 126.

‡ Nadeau and Branchen, *J. Amer. Chem. Soc.*, 1935, 57, 1363.

§ Cf. La Mer and Downes, *ibid.*, 1931, 53, 888.

of strong base (MOH) has been added to the mixed acids. Applying the law of mass action *

$$\begin{aligned} & \frac{[\text{H}^+][\text{A}_\text{I}']}{[\text{HA}_\text{I}]} = k_\text{I} \quad \dots \quad (\text{xxxix}) \\ \text{and} \quad & \frac{[\text{H}^+][\text{A}_\text{II}']}{[\text{HA}_\text{II}]} = k_\text{II} \quad \dots \quad (\text{xxxix}) \end{aligned}$$

Further, if the salts formed when the acids are neutralized are completely ionized, then

$$\begin{aligned} a_\text{I} &= [\text{HA}_\text{I}] + [\text{A}_\text{I}'] \quad \dots \quad (\text{xxxix}) \\ \text{and} \quad a_\text{II} &= [\text{HA}_\text{II}] + [\text{A}_\text{II}'] \quad \dots \quad (\text{xxxix}) \end{aligned}$$

Since the solution is electrically neutral the sum of all the positive charges must balance the negative charges; hence

$$[\text{M}'] + [\text{H}^+] = [\text{A}_\text{I}'] + [\text{A}_\text{II}'] + [\text{OH}'] \quad \dots \quad (\text{xxxix})$$

If both base and salts are completely ionized, $[\text{M}'] = b$, and if hydrolysis is small, which is generally the case except very close to the equivalence point, $[\text{OH}']$ may be neglected; therefore

$$b + [\text{H}^+] = [\text{A}_\text{I}'] + [\text{A}_\text{II}'] \quad \dots \quad (\text{xxxix})$$

By means of equations (xxxix) and (xxxix), $[\text{A}_\text{I}']$ and $[\text{A}_\text{II}']$ may be expressed in terms of $[\text{H}^+]$ and k_I or k_II , and by substitution in equation (xxxix) it follows that

$$[\text{H}^+] = \frac{a_\text{I}k_\text{I}}{[\text{H}^+] + k_\text{I}} + \frac{a_\text{II}k_\text{II}}{[\text{H}^+] + k_\text{II}} - b \quad \dots \quad (\text{xxxix})$$

This cubic equation enables the value of $[\text{H}^+]$ at any stage of the neutralization to be calculated, but the solution is not simple. A special case can be examined, however, by an approximate treatment. Suppose the base has been added in an amount equivalent to that of the stronger acid, say HA_I , then $a_\text{I} = b$; substituting for b in equation (xxxix), and neglecting all terms involving $[\text{H}^+]^2$, $[\text{H}^+]^2k_\text{I}$, $[\text{H}^+]^2k_\text{II}$ and $[\text{H}^+]k_\text{I}k_\text{II}$, since they are likely to be very small for weak acids, it is found that

$$a_\text{I}[\text{H}^+]^2 + k_\text{II}(a_\text{I} - a_\text{II})[\text{H}^+] - a_\text{II}k_\text{I}k_\text{II} \approx 0 \quad \dots \quad (\text{xxxix})$$

If a_I and a_II are not very greatly different, and k_II is small, the second term of the left-hand side may be neglected; then

$$[\text{H}^+] \approx \sqrt{a_\text{II}k_\text{I}k_\text{II}/a_\text{I}} \quad \dots \quad (\text{xxxix})^\dagger$$

For the special case in which the initial concentrations of the two acids are equal, i.e. $a_\text{I} = a_\text{II}$, then

$$[\text{H}^+] \approx \sqrt{k_\text{I}k_\text{II}} \quad \dots \quad (\text{xli})$$

$$\text{pH} = \frac{1}{2}\text{p}k_\text{I} + \frac{1}{2}\text{p}k_\text{II} \quad \dots \quad (\text{xli})$$

* As the treatment given here is approximate, activity coefficients have been neglected; the method is, however, exactly the same if these coefficients are included.

† See also, Roller, *ibid.*, 1932, 54, 3485.

at the first equivalence point. Thus for a mixture containing equivalent amounts of acetic acid ($k = 1.8 \times 10^{-5}$) and propionic acid ($k = 1.4 \times 10^{-5}$) the hydrogen ion concentration at this equivalence point is 1.6×10^{-5} i.e. pH 4.8; for acetic acid alone the pH at the equivalence point, for a 0.1*N*-solution, is 8.87. This result is important, as it indicates a definite flattening of the pH -neutralization curve of the mixture in the vicinity of the first equivalence point (cf. Fig. 16, p. 232). The extent of this flattening depends on the ratio of the hydrogen ion concentration at the equivalence point in the single (stronger) acid solution, represented by $[H^+]$, to that at the first equivalence point in the mixed solution, $[H^+]_m$. Now

$$[H^+] = \sqrt{k_w k_I / a_I}, \text{ equation (xiv), p. 219,}$$

and

$$[H^+]_m = \sqrt{k_I k_{II}}$$

$$\frac{[H^+]}{[H^+]_m} = \sqrt{k_w / a_I k_{II}} \quad (\text{xlii})$$

If k_{II} is large then the difference between $[H^+]$ and $[H^+]_m$ will be considerable, and the pH -neutralization curve will not show any appreciable inflexion at the first equivalence point; the smaller the value of k_{II} , however, the closer will $[H^+]$ and $[H^+]_m$ be to one another, and so the first part of the neutralization curve for the mixture approaches that for the single acid. Since k_I must be fairly large ($> 10^{-7}$) in order that its pH -neutralization curve may show a definite inflexion, it follows that if the curve for the mixture is also to show an inflexion at the point when the stronger acid is neutralized the ratio of k_I/k_{II} must be as large as possible. According to the deductions of Auerbach and Smolczyk* k_I/k_{II} must be at least 16, for the slightest inflexion to be visible, and in order that the curve may be of value for analytical purposes (see p. 262) the ratio must be greater than 10^4 .†

In general when an acid is neutralized to the extent of 1 per cent. (see equation ix),

$$\begin{aligned} pH &= pk_a + \log 1/99 \\ &\approx pk_a - 2. \end{aligned}$$

Hence neutralization of the weaker acid in a mixture may be regarded as commencing when the pH is equal to $pk_{II} - 2$; at this point the pH -neutralization curve for the mixture will com-

* *Z. physikal. Chem.*, 1924, **110**, 65; see also Kilpi, *ibid.*, 1935, **175**, 239.

† See also Tizard and Boeree, *J. Chem. Soc.*, 1921, **99**, 132; Kolthoff and Furman, *Indicators*, 1926, p. 121 *et seq.*; Britton, *Hydrogen Ions*, 1932, p. 160.

mence to diverge from that of the stronger acid. Similarly when an acid is 99 per cent. neutralized

$$\begin{aligned} pH &= pk_a + \log 99/1 \\ &\approx pk_a + 2. \end{aligned}$$

The neutralization of the stronger acid may, therefore, be regarded as complete when the pH of the mixture is $pk_I + 2$; if this is less than $pk_{II} - 2$, the neutralization curve of the weaker acid will have no appreciable effect on that of the stronger. Hence if $pk_{II} - pk_I > 4$, i.e. $k_I/k_{II} > 10^4$, the curve for the mixture will show no appreciable divergence from that of the separate acids; the inflexion at the first equivalence point will then be as definite as in the single acid.

The same arguments apply if the two acids are not present in equivalent concentrations; in this case it may be shown that a small concentration of the weaker acid favours the formation of the first inflexion.

When the second equivalence point is being approached the pH -neutralization curve has an inflexion dependent on the ionization constant and on the concentration of the weaker acid; the smaller the constant, and the concentration, the less marked will be the inflexion. The pH at the final end-point may be calculated from the equation $[H^+] = \sqrt{k_w k_{II}/a_{II}}$, which applies to a solution of a salt of the acid HA_{II} . On the whole it may be concluded that the first equivalence point is distinct if $k_I > 10^{-7}$, $k_I/k_{II} > 10^4$ and a_I/a_{II} is large; the inflexion for complete neutralization is distinct if $k_{II} > 10^{-7}$ and a_{II} is not less than $0.01N$.

A satisfactory idea of the complete neutralization curve for a mixture of acids may be obtained, in most cases, by plotting the curves for the two acids separately side by side: the curve for the stronger acid being on the left (Fig. 16). The two curves are then connected by their common tangent, and a very close approximation to the pH -neutralization curve of the mixture results (ABC); in order to fix the portion between the two separate curves more closely, use may be made of the pH at the first equivalence point calculated by means of equation (xxxix).

The flattening of the neutralization curves may be considered from another standpoint: when a base is added to a mixture of acids it distributes itself between them in amounts roughly proportional to their dissociation constants and their concentrations (see p. 99). If one acid is much stronger than the other, or present in great excess, or both, it will be almost completely neutralized before the other acid commences to be neutralized. The pH -neutralization curve for the mixture will thus follow that of the stronger acid almost to its complete neutralization, and hence will

show a distinct break at the first equivalence point. If the two acids have ionization constants of comparable magnitude they will be neutralized simultaneously to more or less the same extent, and there can be no rapid change of pH until both acids are almost completely neutralized; the curve, therefore, has no inflexion at the first equivalence point.

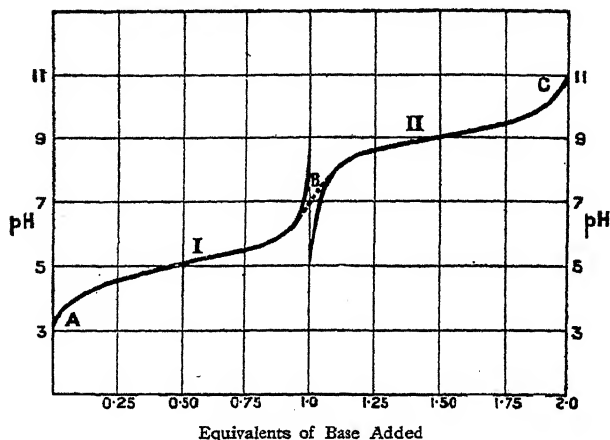
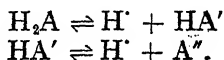


FIG. 16.—Neutralization curve of a mixture of two acids

Neutralization of Dibasic Acids by a Strong Base—

A weak dibasic acid behaves on neutralization to some extent like a mixture of equivalent amounts of two weak monobasic acids; there is, however, an important difference. If the dibasic acid is H_2A , then the two monobasic acids may be regarded as H_2A and HA' , which ionize:



In the initial acid solution the concentration of HA' will be small, as H_2A is only slightly ionized; as neutralization proceeds, however, the salt MHA is formed and this is almost completely ionized into M' and HA' ions. The concentration of the second, or weaker, acid HA' , thus increases—up to a certain point—during the titration; in this respect the behaviour differs from a mixture of two independent acids. The variation of pH in the course of neutralization may be calculated by a method similar to that applied to the case of mixed acids.*

* Cf. Noyes, *Z. physikal. Chem.*, 1893, **11**, 495; Auerbach and Smolczyk, *loc. cit.*; Britton, *J. Chem. Soc.*, 1925, 127, 1896.

Let k_1 and k_2 be the first and second dissociation constants of the dibasic acid, hence

$$k_1 = [\text{H}'] [\text{HA}'] / [\text{H}_2\text{A}] \text{ and } k_2 = [\text{H}'] [\text{A}'''] / [\text{HA}']^*.$$

If a is the initial concentration of the acid in gm. mols. per litre, and the salts MHA and M_2A formed by the addition of a mono-acid base MOH are completely ionized, then

$$a = [\text{H}_2\text{A}] + [\text{HA}'] + [\text{A}'''] \quad \dots \quad (\text{xliii})$$

For *electrical* neutrality

$$[\text{M}'] + [\text{H}'] = [\text{HA}'] + 2[\text{A}'''] + [\text{OH}']. \quad \dots \quad (\text{xliv})^\dagger$$

Since both salts are completely ionized, $[\text{M}'] = b$, the gm. equivs. of base added at any given instant. Eliminating $[\text{H}_2\text{A}]$, $[\text{HA}']$ and $[\text{A}''']$, it is found that

$$\frac{b + [\text{H}'] - [\text{OH}']}{[\text{H}'] + 2k_2} = \frac{ak_1}{[\text{H}']^2 + k_1[\text{H}'] + k_1k_2} \quad \dots \quad (\text{xlv})$$

If $[\text{OH}']$ is replaced by $k_w/[\text{H}']$ the equation involves $[\text{H}']^4$, and a solution is difficult. When the extent of hydrolysis is small, during the first part of the neutralization, $[\text{OH}']$ may be neglected; the resulting equation is a cubic and cannot easily be solved for $[\text{H}']$, although it may be used in some circumstances.

The special case may be considered of the hydrogen ion concentration at the first equivalence point, that is when sufficient base has been added to neutralize half the total acid and a is equal to b . If the acid is moderately strong in both stages then the pH at the first equivalence point will be less than 7; it is then possible to neglect $[\text{OH}']$ in comparison with $[\text{H}']$, and putting $a = b$, equation (xlv) reduces to

$$[\text{H}']^2 = \frac{k_1k_2(a - [\text{H}'])}{a + k_1 + [\text{H}']} \quad \dots \quad (\text{xlvi})$$

Since $[\text{H}']$ is generally small it may be neglected in comparison with a ; hence

$$[\text{H}']^2 \approx \frac{k_1k_2a}{a + k_1} \quad \dots \quad (\text{xlvia})$$

This equation not only gives the hydrogen ion concentration at the first equivalence point, but also, what comes to the same thing, that in a solution of the acid salt MHA.

* In the approximate treatment given here activity coefficients are assumed to be equal to unity; for the more rigid method see Morton, *Trans. Faraday Soc.*, 1928, 24, 14. For extension to acids of higher basicity, see Maxwell and Partington, *ibid.*, 1935, 31, 922. See also Murali, *J. Amer. Chem. Soc.*, 1930, 52, 3518; Söderback, *Arkiv Kemi, Min., Geol.*, 1933, 11 A, No. 8, 1.

† The term $2[\text{A}''']$ applies here since each A''' ion carries *two* negative charges.

When the first stage of the acid is weak, or the first strong and the second very weak, the equivalence point is near pH 7 and so $[H'] - [OH']$ may be neglected and equation (xlv) becomes

$$[H'] = \sqrt{k_1 k_2} \quad \dots \quad (xlvii) *$$

If both stages of the acid are weak then it is probably justifiable at the first equivalence point to neglect $[H']$ in comparison with $[OH']$ on the left-hand side of equation (xlv): it then reduces to a cubic, but if the term $k_1 k_2 k_w$ is neglected as being extremely small it becomes a quadratic, and

$$[H'] = \frac{1}{2a}(k_w + \sqrt{k_w^2 + 4ak_1 k_w + 4a^2 k_1 k_2}) \quad (xlviii)$$

For a 0.1N-solution of carbonic acid, taking k_1 as 3×10^{-7} and k_2 as 6×10^{-11} , the value of $[H']$ is 4.24×10^{-9} gm. ion per litre; the difference between the solutions of equations (xlvii) and (xlviii) are inappreciable, although $[H']$ and $[OH']$ are not equal.

The presence of an inflexion at the first equivalence point in the pH -neutralization curve of a dibasic acid depends, as for a mixture of two monobasic acids, on the ratio of k_1 to k_2 . According to Auerbach and Smolczyk, k_1/k_2 must be at least 16 before the titration curve shows the slightest inflexion,[†] and for the inflexion to be sufficiently marked for analytical application k_1/k_2 must be at least 10,000. Succinic and tartaric acids, for which k_1/k_2 is about 17 and 13 respectively, on neutralization yield a continuous pH curve, without inflexion, until the whole of the acid is neutralized; oxalic and malonic acids, however, show slight inflexions at the first equivalence point, since k_1/k_2 is 1269 and 476 respectively.[‡] All these acids show marked inflexions at the second equivalence point, since k_2 in every case is greater than 10^{-6} . For carbonic acid k_1/k_2 is 5×10^3 , so the inflexion at the first equivalence point will be quite evident, but it will be almost negligible at the second as k_2 is only 6×10^{-11} . In the neutralization of chromic acid there are distinct inflexions at both equivalence points, since the first ionization stage of chromic acid is that of a strong acid, and the second ionization constant is about 1.3×10^{-4} .[§] If both ionization stages of a dibasic acid are those of a strong acid, e.g. sulphuric acid, the neutralization curve will not show an inflexion until the second equivalence point is reached. The general tendency of the pH -neutralization curves may be represented quite satisfactorily by the method used for a mixture of acids; the curves for the separate stages may be drawn side by side, from the known dissociation constants, and then joined by a tangent.

* For equations involving activity coefficients, see Morton, *loc. cit.*

† See also Kilpi, *Z. physikal. Chem.*, 1935, 174, 441.

‡ Britton, *loc. cit.*

§ Britton, *J. Chem. Soc.*, 1924, 125, 1572.

Distribution of Base between the Stages of a Dibasic Acid—In order to determine the relative amounts of first and second stage ionizations involved at any point in the neutralization of a dibasic acid, use may be made of the formulæ derived by Michaelis.* The total concentration of dibasic acid is equal to $[H_2A] + [HA'] + [A'']$ (equation xliii, p. 233), then

$$\alpha_1 = \frac{[HA']}{[H_2A] + [HA'] + [A'']} \text{ and } \alpha_2 = \frac{[A'']}{[H_2A] + [HA'] + [A'']} \quad (\text{xlix})$$

where α_1 represents approximately the fraction of acid neutralized *only* in the first stage, and α_2 that in the second stage. Since $k_1 = [H'] [HA'] / [H_2A]$ and $k_2 = [H'] [A''] / [HA']$, then

$$\alpha_1 = \frac{[HA']}{[H'] [HA'] / k_1 + [HA'] + [HA'] k_2 / [H']} \quad (I)$$

$$[H'] / k_1 + 1 + k_2 / [H']$$

$$\text{Similarly } \alpha_2 = \frac{[H']}{[H'] / k_2 + 1 + [H']^2 / k_1 k_2} \quad (\text{li})$$

The extent of neutralization of the second stage obviously increases as $[H']$ decreases; for a given pH the amount of this neutralization is small if k_2 is small. The point at which α_1 is a maximum is of some interest; it is best determined by considering $1/\alpha_1$, thus:

$$\frac{1}{\alpha_1} = 1 + \frac{[H']}{k_1} + \frac{k_2}{[H']} \quad (\text{lii})$$

Differentiating with respect to $[H']$,

$$\frac{d\left(\frac{1}{\alpha_1}\right)}{d[H']} = \frac{1}{k_1} - \frac{k_2}{[H']^2}$$

For α_1 to be a maximum, $1/\alpha_1$ must be a minimum, and the differential coefficient must equal zero; therefore,

$$\frac{1}{k_1} = \frac{k_2}{[H']^2}$$

and

$$[H'] = \sqrt{k_1 k_2} \quad (\text{liii})$$

It has already been shown that as a general rule $[H'] \approx \sqrt{k_1 k_2}$ at the first equivalence point; hence under these conditions α_1 is a maximum at this point.

* See *Hydrogen Ion Concentration*, Eng. trans., 1926, p. 55; for treatment involving activities and extension to acids of higher basicity, see references on p. 233 *supra*.

Neutralization of a Tribasic Acid by a Strong Base

The method of calculating the variation of hydrogen ion concentration during neutralization is the same as that used for a dibasic acid; the resulting equation is, however, much more complicated. Auerbach and Smolczyk * have deduced that at the first equivalence point

$$[\text{H}^+]_1^2 = k_1 k_2 \frac{2k_3 + [\text{H}^+]_1}{[\text{H}^+]_1} \approx k_1 k_2 \quad \dots \quad (\text{liv})$$

if k_3 is small, and at the second equivalence point

$$[\text{H}^+]_2^2 = k_2 k_3 \quad \dots \quad (\text{lv})$$

These relationships are only approximate,† but they can be used to give a rough indication of the pH's at the two intermediate equivalence points. The pH at the final neutralization point may be calculated from the equation giving the hydrogen ion concentration in a hydrolysed salt solution, k_3 being the appropriate value for k_a . The conditions for inflexions in the curve are the same as for dibasic acids; the first inflexion depends on k_1/k_2 , and the second on k_2/k_3 , whereas the final inflexion depends on k_3 and the concentration of the solution. For phosphoric acid k_1 is 1.0×10^{-2} , k_2 is 1.4×10^{-7} and k_3 is 2×10^{-12} approximately; hence k_1/k_2 is 7×10^4 , and k_2/k_3 is also 7×10^4 . The pH-neutralization curve should, therefore, have a distinct inflexion at the first and second equivalence points, corresponding to the formation of NaH_2PO_4 and Na_2HPO_4 , respectively. The third equivalence point will not be marked by any appreciable inflexion since k_3 is so small.‡ The pH values at the first two equivalence points may be calculated as 4.43 and 9.28 respectively, and that at the third as about 12.35 for 0.1N-solution; these results are in agreement with experimental observations. As in the neutralization of a dibasic acid the general tendency of the pH-neutralization curve may be determined by drawing the three separate curves for the three stages of ionization from the known values of k_1 , k_2 and k_3 , and then connecting up the curves by means of tangents; the equivalence points may be fixed by the approximate equations given here.

Mixtures of Acids—The trend of the neutralization curve for any mixture of acids may be obtained by drawing the separate curves for the different stages of each acid in order of decreasing ionization constants, and then joining up by means of tangents. If a series of acids is chosen such that the ratio of the successive

* *loc. cit.*

† See Morton, *loc. cit.*

‡ By working with a saturated solution of Na_2HPO_4 and concentrated alkali the inflexion at the third equivalence point has been detected (Hahn and Klockmann, *Z. physikal. Chem.*, 1930, 151, 80).

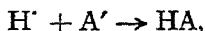
ionization constants is never very large, all inflexions may be avoided. Thus Prideaux and Ward* worked with a mixture of phosphoric, phenyl acetic and boric acids, for which the ionization constants, in order, are given as

Phosphoric Acid. 1st stage.	Phenyl Acetic Acid.	Phosphoric Acid. 2nd stage.	Boric Acid.	Phosphoric Acid. 3rd stage.
1.1×10^{-2}	5.4×10^{-5}	1.41×10^{-7}	6×10^{-10}	3×10^{-12}

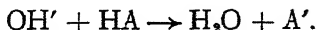
On neutralization the pH varied continuously from 2 to 12, without any appreciable inflexion, since k_n/k_{n+1} was never greater than about 400. Even less inflexion is evident when a mixture consisting of citric acid, diethyl-barbituric acid, boric acid and potassium dihydrogen phosphate is neutralized.†

Neutralization of Mixed and Di-acid Bases—The neutralization of a mixture of two mono-acid bases or of a di-acid base by means of a strong acid may be treated in exactly the same manner as the neutralization of acids by a strong base. If $[H']$ is replaced by $[OH']$ and k_a by k_b , the same formulæ are applicable, and the criteria for inflexions at the first and second equivalence points are analogous to those deduced for acids. The pH -neutralization curves may also be built up by placing the separate curves side by side in the appropriate order.

Buffer Solutions—Aqueous solutions of both sodium chloride and of ammonium acetate have a pH of about 7, but the addition of 1 c.c. of 0.1*N*-hydrochloric acid to a litre of solution alters the pH to 4, in the former case, and hardly affects it in the latter. The resistance to change in the hydrogen ion concentration of a solution on the addition of acid or alkali is known as **buffer action**,‡ and buffer solutions almost invariably consist of a mixture of a weak acid, or a weak base, and its salt.§ Buffer action in a solution of a weak acid and its salt is explained by the fact that hydrogen ions are removed by anions of a weak acid to form un-ionized molecules, thus :



which is neutralization in its widest sense, since the anions are basic. Hydroxyl ions are also removed by neutralization, according to the equation :



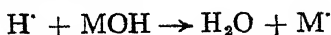
* *J. Chem. Soc.*, 1924, 125, 426.

† Britton and Robinson (R. A.) *ibid.*, 1931, 1456.

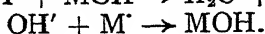
‡ See Sørensen, *Biochem. Z.*, 1909, 21, 131, 201; *Compt. rend. Lab. Carlsberg*, 1909, 8, 28. The solutions of buffers have been also called 'regulator mixtures', and said to possess 'reserve acidity and alkalinity'.

§ In general terms it may be said that a mixture of any weak acid, or base, with its conjugate base, or acid, constitutes a buffer system.

If the buffer solution is a mixture of a weak base and its salt the corresponding equations* are :



and



In the solution of a strong acid, or base, and its salt buffer action is very limited ; it is in fact due only to the water used as solvent (p. 244).

A useful idea of buffer capacity can be obtained from a study of the *pH*-neutralization curves of various acids ; these curves may be regarded as showing the variation of *pH* in a mixture of acid, or base, and its salt as the result of the further addition of base (i.e. left to right in the diagram), or acid (i.e. right to left). An examination of Figs. 13 and 14 shows that 0.1*N*-hydrochloric acid, partly neutralized, may be regarded as having buffer capacity within the range of *pH* 1 to 2, since the *pH* varies gradually only within these limits ; similarly 0.1*N*-sodium hydroxide can act as a buffer between *pH* 13 and 14. A partly neutralized solution of 0.1*N*-acetic acid, on the other hand, should exert marked buffer action between *pH* 4 and 6, and even to some extent from *pH* 3 to 4. A mixture of 0.1*N*-ammonium hydroxide and hydrochloric acid, in the same way, should have definite buffering power between *pH* 9 and 11. In the neutralization of a weak acid with a strong base, or vice versa, there is generally a definite inflexion at the equivalence point ; hence the salt formed cannot be regarded as a very good buffer. If the weak constituent is *very* weak, or both constituents are weak, there is no appreciable inflexion, and a gradual change of *pH* is observed ; salts of such acids and base are good buffers. For this reason ammonium acetate can be regarded as a buffer, whereas the sodium salt alone has little buffer effect.

In many aspects of chemical work † it is necessary to have solutions of known hydrogen ion concentration ; such solutions could be made by diluting a standard solution of acid or alkali until the required *pH* was reached. The solutions would, however, be greatly affected by alkali dissolved from the glass vessels, and by carbon dioxide absorbed from the air, and the hydrogen ion concentrations could not be kept constant. In such cases buffer solutions are used, as they are not only very little affected by slight amounts of acidic and basic impurities, but they also resist any tendency towards a change of hydrogen ion concentration as a result of reactions occurring in the buffer medium. For example,

* In the general case where B is the base and BH^+ the cation in its salt, the equations are $\text{H}^+ + \text{B} \rightarrow \text{BH}^+$, and $\text{OH}^- + \text{BH}^+ \rightarrow \text{B} + \text{H}_2\text{O}$. Here, as elsewhere, H^+ represents the H_3O^+ ion.

† For full account see Clark, *The Determination of Hydrogen Ions* ; Britton, *Hydrogen Ions* ; Smith, *Analytical Processes*.

in the electrolysis of many solutions hydrogen ions are discharged at the cathode, and the solution in the vicinity of this electrode tends to become alkaline; if a buffer solution is used, however, the rate of change of hydrogen ion concentration is much reduced. Although the buffering action of partly neutralized solutions of weak acids has been known and applied for some time,* the first quantitative treatment of the subject appears to have been made by Henderson† and is based on the application of the law of mass action.‡ In the mixture of a weak acid and its salt the equilibrium may be represented by exactly the same equations as used in the study of the neutralization of an acid (p. 217); hence it follows that for a buffer solution of a weak acid and its salt with a strong base:

$$pH = pK_a + \log [\text{salt}]/[\text{acid}] + \log f_A \quad (\text{Ivi})$$

if the pH is not less than 4. Similarly for a weak base and its salt with a strong acid,

$$pOH = pK_b - pH = pK_b + \log [\text{salt}]/[\text{base}] + \log f_M \quad (\text{Ivii})$$

if the pH is not greater than 10. Sometimes a buffer solution is made up of two salts representing different stages of neutralization of a polybasic acid, e.g. Na_2HPO_4 and NaH_2PO_4 . The latter salt is regarded as completely ionized thus



and the $\text{H}_2\text{PO}_4'$ ionizes further as a weak acid; the Na_2HPO_4 is regarded as the sodium salt of this acid. The ionic equilibrium of the acid is



and by the law of mass action

$$K_2 = \frac{[\text{H}^+][\text{HPO}_4'']}{[\text{H}_2\text{PO}_4']} \cdot \frac{f_H f_2}{f_1},$$

where K_2 is the second stage (true) dissociation constant of phosphoric acid, and f_1 and f_2 the activity coefficients of the $\text{H}_2\text{PO}_4'$ and HPO_4'' ions, respectively. Rearranging the terms and taking logarithms, it is found that

$$pH = pK_2 + \log [\text{HPO}_4'']/[\text{H}_2\text{PO}_4'] + \log f_2/f_1 \quad (\text{Iviii})$$

* See Fernbach and Hubert, *Compt. rend.*, 1900, 131, 293; Fels, *Z. Elektrochem.*, 1904, 10, 208; Moore, Roaf and Whitley, *Proc. Roy. Soc.*, 1905, 77 B, 102.

† *Amer. J. Physiol.*, 1908, 21, 173; *J. Amer. Chem. Soc.*, 1908, 30, 954; see also Washburn, *ibid.*, p. 31.

‡ The original treatment did not involve activities, but concentrations.

If the salts are assumed to be completely dissociated the equation may be written :

$$pH = pK_2 + \log [Na_2HPO_4]/[NaH_2PO_4] + \log f_2/f_1 \quad . \quad . \quad (lix)$$

In general the useful range of a buffer solution lies between pH values of $pK \pm 1$ (see Figs. 14-16); hence in order to cover the whole range of hydrogen ion concentrations a series of acids, and their salts, are required. In Table XXXVIII (p. 242) will be found a list of buffer solutions which have been suggested by various workers.*

Reference has already been made (p. 237) to the fact that on neutralization the pH of mixtures of certain acids varies gradually and the pH-neutralization curve shows no marked inflexion between pH 2 and 12. Such acids have been proposed for preparing 'universal buffer mixtures'; † by adding various pre-determined amounts of alkali, buffer solutions of any desired pH from 2 to 12 may be obtained. The buffer solutions containing a mixture of one weak acid and the salt of another ‡ are equivalent to a system of two acids and their salts. Thus di-sodium phosphate and citric acid is equivalent to a mixture of NaH_2PO_4 ($k_2 = 1.4 \times 10^{-7}$), its salt (Na_2HPO_4), citric acid ($k_1 = 10^{-3}$; $k_2 = 2.5 \times 10^{-5}$ and $k_3 = 1.5 \times 10^{-6}$), and one or more of its salts; the pH range of this buffer can thus be from pK_1 (citric acid) - 1, i.e. pH 2, to pK_2 (phosphoric acid) + 1, i.e. pH 8.

Although the pH of a simple buffer solution may be determined approximately by the use of the Henderson equation, omitting activity coefficients, the results are not sufficiently reliable for accurate work; the hydrogen ion 'concentrations' of all buffer solutions must, therefore, be checked by means of the hydrogen electrode (p. 385). It has been found, however, that such values only hold for the particular solution studied, and the addition of neutral salts, which presumably have no influence on the ionic equilibrium, and dilution have a marked effect on the pH; these deviations are not to be expected from the Henderson equation :

$$pH = pK_a + \log [\text{salt}]/[\text{acid}] \quad . \quad . \quad . \quad (lx)$$

and are not even accounted for by the modified form which includes the value of $[H^+]$. If allowance is made, however, for the activity coefficient of the anion of the salt (f_A) the explanation of the anom-

* For further details and methods of preparation of the reagents involved, consult the papers cited, or Clark, *op. cit.*, 1928, p. 192 *et seq.*; Kolthoff and Furman, *Indicators*, 1926, p. 22 *et seq.*; Britton, *op. cit.*, 1932, p. 217 *et seq.*; Kolthoff, *Säure-Basen Indikatoren*, 1932.

† Prideaux and Ward, *J. Chem. Soc.*, 1924, 125, 426; Britton and Robinson (R. A.), *loc. cit.*; see also Michaelis, *Biochem. Z.*, 1931, 234, 139; Thiel *et al.*, *Z. Elektrochem.*, 1934, 40, 150.

‡ See McIlvaine, *loc. cit.*; Kolthoff, *loc. cit.*

alies is apparent; the value of this coefficient depends on the 'ionic strength' of the medium (p. 116), and hence it, and the pH , will be influenced by neutral salts and by dilution.*

By means of the Debye-Hückel equation (p. 143) it is possible to express the activity coefficient of an ion in terms of the ionic strength of the solution, and hence a modified, and more accurate, form of the Henderson equation may be obtained. According to the deductions of Debye and Hückel the activity coefficient (f) of an ion in aqueous solution at 25° is given by the expression

$$-\log f = \frac{0.5z^2\sqrt{\mu}}{1 + B_1\sqrt{\mu}} - C\mu \quad (\text{lx})^\dagger$$

where z is the valency of the ion and B_1 and C are constants. This may be written in the form

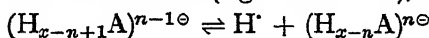
$$-\log f = 0.5z^2\sqrt{\mu} - C'\mu \quad (\text{lxii})$$

where C' is a constant approximately equal to $0.5z^2B_1 + C$ (see p. 143). The accurate form of the Henderson equation for a monobasic acid and its salt, at pH 's greater than 4, is

$$pH = pK_a + \log [\text{salt}]/[\text{acid}] + \log f_A \quad (\text{lvi})$$

$$= pK_a + \log [\text{salt}]/[\text{acid}] - 0.5\sqrt{\mu} + C'\mu \quad (\text{lxiii})$$

If the buffer consists of a mixture of two salts of a polybasic acid, e.g. NaH_2PO_4 and Na_2HPO_4 , the equation requires slight modification, as the activity coefficients of both species must be included. Let H_xA represent the polybasic acid, and suppose the buffer consists of the salts $M_{n-1}H_{x-n+1}A$ (salt I) and $M_nH_{x-n}A$ (salt II), where M is a univalent cation (e.g. Na^+ or K^+), then



and

$$pH = pK_n + \log [(H_{x-n}A)^{n\ominus}]/[(H_{x-n+1}A)^{n-1\ominus}] + \log f_n/f_{n-1} \quad (\text{lxiv})$$

where pK_n is the exponent of the n th ionization constant of the acid. If the salts may be taken as completely ionized, and the values for the activity coefficients are obtained from the formula given, then

$$\begin{aligned} pH &= pK_n + \log [\text{salt II}]/[\text{salt I}] - 0.5\{(n)^2 - (n-1)^2\}\sqrt{\mu} + C'\mu \\ &= pK_n + \log [\text{salt II}]/[\text{salt I}] - (n-0.5)\sqrt{\mu} + C'\mu \quad (\text{lxv}) \end{aligned}$$

* See Michaelis, *et al.*, *Biochem. Z.*, 1921, **119**, 307; 1923, **141**, 394; Warburg, *Biochem. Z.*, 1922, **16**, 153; Hastings and Sendroy, *J. Biol. Chem.*, 1925, **65**, 445; Cohn, *et al.*, *J. Amer. Chem. Soc.*, 1927, **49**, 173; 1928, **50**, 696; Morton, *J. Chem. Soc.*, 1928, 1401; Robinson (H. W.), *J. Biol. Chem.*, 1929, **82**, 775; Kolthoff, *Rec. trav. chim.*, 1927, **46**, 430; 1928, **47**, 558, 819, 826; Ölander, *Z. physikal. Chem.*, 1929, **144**, 49; Green, *J. Amer. Chem. Soc.*, 1933, **55**, 2331.

† This is equation (xxvi), p. 143 of Chap. VII.

TABLE XXXVIII
BUFFER SOLUTIONS *

Mixture.	pH range.	Reference.
Sodium Acetate and Hydrochloric Acid	0.65- 5.20	Walpole, <i>Biochem. Z.</i> , 1914, 105, 2501, 2521.
Potassium Chloride and Hydrochloric Acid	1.00- 2.20	Clark and Lubs, <i>J. Bact.</i> , 1917, 2, 1, 109, 191.
Glycine and Hydrochloric Acid	1.04- 3.68	Sørensen, <i>Ergeb. Physiol.</i> , 1912, 12, 393.
Disodium Hydrogen Citrate and Hydrochloric Acid	1.04- 4.96	Sørensen, <i>loc. cit.</i>
Potassium Acid Phthalate and Hydrochloric Acid	2.2- 3.8	Clark and Lubs, <i>loc. cit.</i>
Sodium Phenylacetate and Phenylacetic acid	3.2- 4.9	German and Vogel (A. I.), <i>J. Chem. Soc.</i> , 1935, 912
Disodium Hydrogen Phosphate and Citric Acid	2.2- 8.0	McIlvaine, <i>J. Biol. Chem.</i> , 1921, 49, 183; Slotta and Franke, <i>Ber.</i> , 1931, 64, 452
Succinic Acid and Borax . . .	3.0- 5.8	Kolthoff, <i>J. Biol. Chem.</i> , 1925, 63, 135.
Acetic Acid and Sodium Acetate .	3.72- 5.57	Walpole, <i>J. Chem. Soc.</i> , 1914, 105, 2501.
Potassium Acid Phthalate and Sodium Hydroxide	4.0- 6.2	Clark and Lubs, <i>loc. cit.</i>
Disodium Hydrogen Citrate and Sodium Hydroxide	4.96- 6.33	Sørensen, <i>loc. cit.</i>
Sodium Acid Maleate and Sodium Hydroxide	5.2- 6.8	Temple, <i>J. Amer. Chem. Soc.</i> , 1929, 51, 1754.
Potassium Dihydrogen Phosphate and Sodium Hydroxide	5.8- 8.0	Clark and Lubs, <i>loc. cit.</i>
Potassium Dihydrogen Phosphate and Borax	5.8- 9.2	Kolthoff, <i>Biochem. Z.</i> , 1927, 189, 191.
Sodium Dihydrogen Phosphate and Disodium Hydrogen Phosphate	5.91- 8.04	Sørensen, <i>loc. cit.</i>
Boric Acid and Borax . . .	6.77- 9.24	Palitzsch, <i>Biochem. Z.</i> , 1915, 70, 333.
Diethylbarbituric Acid and Sodium Salt	7.0- 9.2	Michaelis, <i>J. Biol. Chem.</i> , 1930, 87, 33.
Borax and Hydrochloric Acid. . .	7.62- 9.24	Sørensen, <i>loc. cit.</i>
Boric Acid and Sodium Hydroxide	7.8- 10.0	Clark and Lubs, <i>loc. cit.</i>
Glycine and Sodium Hydroxide .	8.24- 10.14	Sørensen, <i>loc. cit.</i>
Dimethylglycine (Na salt) and Hydrochloric acid	8.6- 9.6	Michaelis and Schubert, <i>J. Biol. Chem.</i> , 1936, 115, 221.
Borax and Sodium Hydroxide .	9.24- 9.97	Sørensen, <i>loc. cit.</i> ; Naegeli and Tyabji, <i>Helv. Chim. Acta</i> , 1932, 15, 751.
Borax and Sodium Hydroxide .	9.2- 11.0	Kolthoff, <i>loc. cit.</i> , 1927.
Sodium Carbonate and Hydrochloric Acid	10.17- 11.36	Kolthoff, <i>loc. cit.</i> , 1925.
Disodium Hydrogen Phosphate and Sodium Hydroxide	10.97- 12.06	Ringer, <i>Chem. Weekblad</i> , 1909, 6, 446; Kolthoff, <i>loc. cit.</i> , 1927; Naegeli and Tyabji, <i>loc. cit.</i>

* For the influence of temperature on the pH in various buffer solutions, see Sørensen, *Ergeb. Physiol.*, 1912, 12, 393; Clark and Lubs, *J. Biol. Chem.*, 1916 25, 479; Walbum, *Biochem. Z.*, 1920, 107, 219; Kolthoff and Tekelenburg, *Rec trav. chim.*, 1927, 46, 33; Brujevicz and Karpova, *Biochem. Z.*, 1932, 251, 60; Kiehl and Loucks, *Trans. Amer. Electrochem. Soc.*, 1935, 67, 81.

In the case of a mixture of Na_2HPO_4 and KH_2PO_4 , used by Cohn, $x = 3$ and $n = 2$, hence

$$pH = pK_2 + \log [\text{Na}_2\text{HPO}_4]/[\text{KH}_2\text{PO}_4] - 1.5\sqrt{\mu} + C'\mu \quad (\text{lxvi})$$

The value of C' depends on the nature of all the salts present in the buffer solution, whether they form a definite part of the mixture or are neutral salts; it is a constant for a given neutral salt and for a given ratio of $[\text{acid}]/[\text{salt}]$ for each acid, but it appears to vary to some extent with the value of this ratio.* There is no means of calculating C' , and so it must be determined by direct experiment; the methods employed depend on two or more measurements of the pH of the solution containing a constant ratio of $[\text{acid}]/[\text{salt}]$, but of varying ionic strength. From the results pK and C' may be calculated; alternatively pK may be determined by extrapolating the term $pH - \log [\text{salt}]/[\text{acid}]$ for a series of solutions to infinite dilution, when $\mu = 0$, and then C' evaluated. Incidentally it may be mentioned that the application of the accurate Henderson equation and the measurement of the pH by *E.M.F.* methods provides the most accurate method for the determination of the *true* dissociation constant of an acid.

By the use, for interpolation purposes, of an equation similar to (lxv), Cohn and his co-workers † have been able to draw up tables by means which it is possible to prepare buffer solutions of the same ionic strength and varying pH , or of the same pH and varying ionic strength; these solutions contain either acetate or phosphate, and the pH range is 3.6 to 7.6.

Buffer Capacity—The first attempt at expressing quantitatively the buffer capacity of a given solution was made by Koppel and Spiro ‡ and later developed by van Slyke.§ Buffer capacity, or buffer index, (β), is defined as the differential ratio, db/dpH , 'between the increment (in gm. equiv. per litre) of strong base, b , added to a buffer solution and the resultant increment in pH . Increment of strong acid is equivalent to a negative increment of base.' Since the addition of a base increases the pH , and the addition of acid, equivalent to negative base, decreases it, the differential db/dpH is always positive; the greater the value of this ratio the more acid or alkali is required to be added in order to produce a certain change of pH . It may thus be regarded as a quantitative measure of the buffering power of a solution. It is interesting to note that db/dpH represents the reciprocal of the slope, in the mathematical sense, of the pH -neutralization curves (Figs. 13-16); the

* See Cohn, *loc. cit.*

† *loc. cit.*; Green, *loc. cit.*

‡ *Biochem. Z.*, 1914, 65, 409.

§ *J. Biol. Chem.*, 1922, 52, 525; see also Täufel and Wagner, *Biochem. Z.*, 1926, 177, 389.

buffer capacity is, therefore, greatest in those regions where the curve is least inclined to the 'degree of neutralization' axis.

Buffer Capacity of Water *—If a quantity b of strong base MOH is added to water or to a strong acid HA the solution will contain M' , OH' , H' and A' ions, and by the requirement of electrical neutrality,

$$[M'] + [H'] = [OH'] + [A'] \quad \dots \quad (lxvii)$$

Since the base may be assumed to be completely dissociated, $b = [M']$

$$\therefore b = [OH'] - [H'] + [A'] \quad \dots \quad (lxviii)$$

Differentiating with respect to pH , noting that $[A']$ remains constant even when base is added, since both acid and salt are completely ionized,

$$\beta_{H_2O} = \frac{db}{d(pH)} = \frac{d[OH']}{d(pH)} - \frac{d[H']}{d(pH)} \quad \dots$$

Since $[H'] [OH'] = k_w$, it follows that $pH = \log [OH'] - \log k_w$, and

$$\therefore d(pH) = d \log [OH']$$

By definition of pH as $-\log [H']$, it is seen that $d(pH)$ is equal to $-d \log [H']$, and substituting these alternative values for $d(pH)$ in equation (lxix), it is found that

$$\beta_{H_2O} = 2.302([H'] + [OH']) \quad \dots \quad (lxx)^\dagger$$

The same result is obtained by considering the addition of a strong acid to water or to a solution of a strong base. Between pH 2.4 and 11.6 the value of β_{H_2O} is less than 0.01; hence the buffer capacity of water is only appreciable in relatively strong acid or alkaline solutions (see Fig. 17).

Buffer Capacity of a Solution of a Weak Acid and its Salt ‡—Suppose a solution of a weak acid HA and its salt MA is made by adding b equiv. of the base MOH to a solution containing initially a equiv. of acid; then

$$a = [HA] + [A'] \quad \dots \quad (i)$$

$$\text{and} \quad [M'] + [H'] = [A'] + [OH'] \quad \dots \quad (ii)$$

and since b may be put as equal to $[M']$,

$$b = [A'] - [H'] + [OH'] \quad \dots \quad (iii)$$

* This treatment, which is simpler than that of van Slyke, is due to Dr. T. B. Smith.

† If activities had not been neglected in the ionic product of water the value of β_{H_2O} would have been $2.302 ([H']/f_H + [OH']/f_{OH})$; this should be used in concentrated salt solutions and the values of f determined approximately by the Debye-Hückel equation.

‡ Cf. Kilpi, *Z. physikal. Chem.*, 1935, 173, 223.

as shown on p. 218. Since $k_a = [H^+][A^-]/[HA]$, and $[HA]$ is equal to $a - [A^-]$, from equation (i), it follows that

$$[A^-] = ak_a/(k_a + [H^+]) \quad (\text{xxi})$$

Substituting this value of $[A^-]$ in equation (iiia), and differentiating with respect to pH , there is obtained

$$\beta = \frac{db}{d(pH)} = \frac{ak_a/(k_a + [H^+])}{d(pH)} - \frac{d[H^+]}{d(pH)} + \frac{d[OH^-]}{d(pH)} \quad (\text{xxii})$$

and hence

$$\beta = 2.302 \left\{ \frac{ak_a[H^+]}{(k_a + [H^+])^2} + [H^+] + [OH^-] \right\} \quad (\text{xxiii})$$

In Fig. 17 the value of β for various pH 's is plotted for a 0.2M aqueous solution of acetic acid-acetate buffer; the buffer capacity

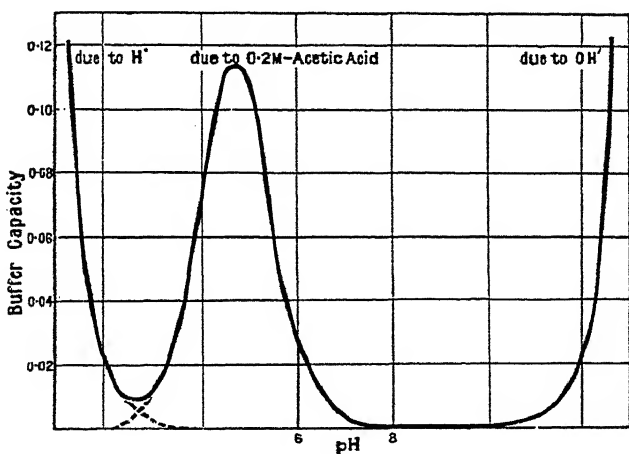


FIG. 17.—Buffer capacity of 0.2M-Acetic acid

of the water itself, as represented by the last two terms, only becomes evident at pH values less than about 3.5 and greater than 10.5. An equation exactly analogous to (xxii), except that k_b replaces k_a , and $[OH^-]$ replaces $[H^+]$ in the first term, and b , used instead of a , is the initial concentration of base, represents the buffer capacity of a mixture of a weak base and its salt. The buffer capacity- pH curves all show a maximum, the position of which can be determined by differentiating the expression for β with respect to $[H^+]$, or pH , and equating to zero. In either case it is found that β is a maximum when $[H^+] = k$, that is when the solution contains equiva-

lent amounts of weak acid, or weak base, and its salt; under these conditions the buffer capacity is

$$\beta = \frac{2.302}{4}a = 0.575a \text{ (for a weak acid and its salt)}$$

$$\text{or } = 0.575b \text{ (for a weak base and its salt)}$$

and is, therefore, directly proportional to the total concentration of the buffer solution.

The buffer capacity of a mixture of acids and their salts is the sum of the separate buffer capacities; thus

$$\Sigma\beta = \beta_1 + \beta_2 + \beta_3 + \dots \quad (\text{xxii})$$

If a number of acids were chosen such that their dissociation constants formed a geometrical progression, with intervals of 10^{-1} , from 10^{-3} to 10^{-11} , the maxima in the separate buffer capacity curves would be very close together, viz. one unit of pH apart; the buffering power of a mixture of these acids in equivalent amounts would then be almost constant, and maximal, over the range from pH 3 to 11. This would constitute an ideal universal buffer system; the mixtures mentioned above are a rough practical approximation.*

Dilution and Neutral Salt Errors—The van Slyke buffer index gives a useful idea of the resistance of a buffer solution to change of pH provided there is no great change in the dilution, and the ionic strength of the medium does not vary appreciably. It is frequently desirable, however, to have a buffer solution which is resistant to pH changes caused by other means than the addition of acid or alkali, e.g. dilution or neutral salts. Morton† has suggested that the power to resist pH changes due to these causes be described by the term $d(pH)/d\sqrt{\mu}$, where μ is the ionic strength of the medium. Since

$$pH = pK + \log [\text{salt}]/[\text{acid}] - 0.5\sqrt{\mu} + C'\mu \quad (\text{viii})$$

$$\frac{d(pH)}{d\sqrt{\mu}} = -0.5 + 2C'\sqrt{\mu}$$

or, in general, for the n th stage of ionization of a polybasic acid

$$\frac{d(pH)}{d\sqrt{\mu}} = -(n - 0.5) + 2C'\sqrt{\mu} \quad (\text{xxiii})$$

The magnitude of the dilution and neutral salt errors thus depends on the basicity of the acid, the ionic strength of the solution, and the constant C' ; the error may be positive, zero or negative, depending on the conditions. In general the smaller the numerical value of $d(pH)/d\sqrt{\mu}$ the more resistant is the buffer solution to pH changes resulting from dilution, or the addition of neutral salts.

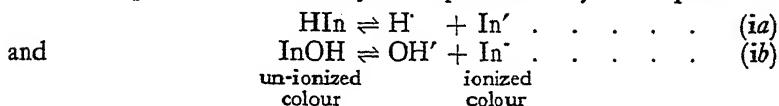
* See Kolthoff and Furman, *Indicators*, 1926, p. 30.

† *J. Chem. Soc.*, 1928, 1401.

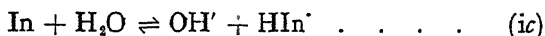
CHAPTER X

INDICATORS

NEUTRALIZATION Indicators—A neutralization indicator is a substance which, within certain limits, varies in colour according to the hydrogen ion concentration of its environment ; it invariably possesses, in some form or another, the properties of a weak acid or a weak base. The first useful theory of indicator action was suggested by Ostwald,* who considered that the un-ionized indicator acid or base had a different colour from that of its ion. Thus, regarding HIn as the general formula of an indicator acid, and InOH that of a base, the equilibria in aqueous solution may be represented by the equations :



If the indicator is an anhydro-base, In , e.g. an amine, then the equilibrium is



which is virtually the same as for the hydrated form InOH .

Consider an acid indicator : as long as it is present in an acid medium its degree of ionization is depressed, and the concentration of In' ions will be very small ; the colour will, therefore, be that of the un-ionized form. If the medium is rendered alkaline, however, the decrease of hydrogen ion concentration will result in further ionization of the indicator and the colour of the ionized form becomes evident. The quantitative relationship between colour and hydrogen ion concentration may be obtained by applying the approximate form of the law of mass action to the indicator equilibrium. Thus

$$\frac{[\text{H}^+][\text{In}']}{[\text{HIn}]} = k \quad . \quad . \quad . \quad . \quad . \quad . \quad (ii)$$

$$\text{and} \quad [\text{H}^+] = k \frac{[\text{HIn}]}{[\text{In}']} \quad . \quad . \quad . \quad . \quad . \quad . \quad (iii)$$

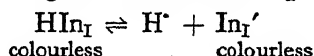
* *Lehrbuch der allgemeinen Chemie*, 1891, Vol. I, p. 791 ; *Z. physikal. Chem.*, 1892, 9, 579 ; see also, Bancroft and Davis (H. L.), *J. Physical Chem.*, 1930, 34, 1797.

If α is the fraction of the total amount of indicator present in the ionized form, then

$$[H] = k^I - \alpha \quad (iv)$$

The actual colour, which depends on the ratio of ionized to un-ionized indicator, is thus directly related to the hydrogen ion concentration. Although this equation expresses satisfactorily the behaviour of indicators with acids, it has been found that the theory requires modification in order to account for the chemical properties of the substances used as indicators. The views outlined below, although more complicated, lead to an equation similar to (iv), and a discussion of the applications of this equation will be deferred until it has been deduced on the basis of the modified theory.

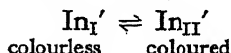
Theory of Indicator Action—As a result of much investigation in organic chemistry concerning the relation between the colour of a compound and its chemical structure, it has been concluded that an indicator consists of two or more tautomeric forms having different constitutional formulæ and different colours. At least one, and frequently more, of these dynamic isomerides, or tautomers, is acidic or basic in nature, and the colour of each ion is the same as that of the un-ionized form of the same structure. Suppose HI_nI is the un-ionized colourless form of the acid indicator: it will ionize to give a colourless In_I' ion, thus



and applying the law of mass action, using concentrations,

$$k_I = [H] [In_I'] / [HI_nI] \quad (v)$$

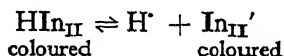
The colourless ion (In_I') will be in tautomeric equilibrium with a coloured ion In_{II}' , the latter having a different structure, viz.



and from the law of mass action

$$k_{II} = [In_{II}'] / [In_I'] \quad (vi)$$

Finally there will be an equilibrium between the coloured ions (In_{II}'), hydrogen ions and the coloured un-ionized molecules (HI_nII), thus



so that

$$k_{II} = [H] [In_{II}'] / [HI_nII] \quad (vii)$$

From equations (v), (vi) and (vii) it may be shown that

$$\frac{[H]([In_I'] + [In_{II}'])}{[HI_nI] + [HI_nII]} = \frac{k_I k_{II}(1 + k_T)}{k_{II} + k_I k_T} = k_{In} \quad (viii)$$

the constant k_{In} replacing the term involving k_{I} , k_{II} and k_{T} . It follows, therefore, that

$$[\text{H}'] = k_{\text{In}} \frac{[\text{HIn}_{\text{I}}] + [\text{HIn}_{\text{II}}]}{[\text{In}_{\text{I}}'] + [\text{In}_{\text{II}}']} \quad \dots \quad (\text{ix})^*$$

If the substance is to be a satisfactory indicator for changes of hydrogen ion concentration, the numerator and denominator of equation (ix) must correspond to two distinct colours; this can only occur if the un-ionized molecules are almost completely either $[\text{HIn}_{\text{I}}]$ or $[\text{HIn}_{\text{II}}]$, and the ions must correspond almost exclusively to the other form. In other words k_{T} must be very small and $k_{\text{I}}/k_{\text{II}}$ large, or vice versa. If this were not the case both numerator and denominator would represent a somewhat similar mixture of both possible colours, and although a change of hydrogen ion concentration would result in a change in the *ratio* of numerator to denominator, there might be no marked alteration in the colour. Equation (ix) for a satisfactory indicator may then be reduced to the form

$$[\text{H}'] = k_{\text{In}} \frac{[\text{un-ionized form}]}{[\text{ionized form}]} = k_{\text{In}} \frac{1 - \alpha}{\alpha} \quad \dots \quad (\text{x})$$

where α is the fraction of the total indicator present as ions; this equation is identical with the one deduced from the simple theory except that (a) the indicator constant k_{In} has a different significance, and (b) the un-ionized and ionized forms considered have different structures. These distinctions, however, do not affect the general application of the relationship.

For a substance to be satisfactory as an indicator it must satisfy the following requirements, in addition to those already mentioned:

- (i) the tautomeric equilibrium must be established very rapidly;
- (ii) the colour change must be due to the tautomeric change only; and
- (iii) the colour change must be determined by the hydrogen ion concentration, and not be appreciably influenced by neutral salts.†

Indicator Range—It may be assumed that when less than, say, 9 per cent. of the total indicator is ionized, i.e. $\alpha = 0.09$, the colour of the ionized form is just barely visible; ‡ the lowest

* Acree, *Amer. Chem. J.*, 1907, 38, 19; Noyes, *J. Amer. Chem. Soc.*, 1910, 32, 815. In the original deduction it was considered that the tautomeric equilibrium existed between the un-ionized molecules HIn_{I} and HIn_{II} ; the viewpoint adopted here of tautomerism of the *ions* is in better harmony with modern ideas in organic chemistry.

† Indicators of a colloidal nature, e.g. congo red, are greatly affected by the presence of electrolytes.

‡ Strictly speaking this should refer to 9 per cent. of the tautomeric forms $\text{HIn}_{\text{I}} + \text{HIn}_{\text{II}}$, but the amount of HIn_{II} may be considered as negligible; nearly all the ions will then be In_{II}' .

hydrogen ion concentration at which the indicator still shows its acid colour (due to HIn_I) will be given by

$$[\text{H}^+] = k_{\text{In}} \frac{0.91}{0.09} = 10k_{\text{In}}$$

or $\text{pH} \approx \text{p}k_{\text{In}} - 1 \quad \dots \dots \dots (\text{xi})^*$

On the other hand, when 91 per cent. of the indicator is in the ionized form ($\alpha = 0.91$), the colour corresponds almost entirely to the completely alkaline condition (due to In_{II}'); the greatest hydrogen ion concentration at which the indicator shows its full alkaline, or ionized, colour is then given by

$$[\text{H}^+] = k_{\text{In}} \frac{0.09}{0.91} \approx 1/10k_{\text{In}}$$

or $\text{pH} \approx \text{p}k_{\text{In}} + 1 \quad \dots \dots \dots (\text{xii})$

Hence as the pH of a solution is increased by adding alkali the colour of an indicator begins to change at a pH equal to $\text{p}k_{\text{In}} - 1$, and is completely changed, as far as the eye can detect, at a pH of $\text{p}k_{\text{In}} + 1$; the transition interval of an indicator is thus approximately two units of pH .† Since various indicators will generally have different values for k_I , k_{II} , and k_T , the values of k_{In} will differ; the range of pH over which the colour changes thus depends on the nature of the indicator.

When the indicator is 50 per cent. ionized, i.e. $\alpha = 0.5$, then

$$[\text{H}^+] = k_{\text{In}}$$

or $\text{pH} = \text{p}k_{\text{In}} \quad \dots \dots \dots (\text{xiii})$

The indicator thus shows a colour exactly intermediate between that of the acid and alkaline forms when the hydrogen ion concentration of the solution is equal to the indicator dissociation constant. This fact suggests a comparatively simple method for determining indicator constants.

Basic Indicators—Indicator bases may be discussed in exactly the same manner as acids; one of the tautomeric un-ionized forms must predominate at equilibrium, and the ions corresponding to the other form must be present in larger concentrations if the colour changes are to be marked. In aqueous solution the relationship between $[\text{OH}^-]$ and the ionized and un-ionized forms may be written :

$$[\text{OH}^-] = k_{\text{In}} \frac{1 - \alpha}{\alpha} \quad (\text{xiv})$$

* The activity coefficient of the hydrogen ions is assumed to be unity.

† This holds for indicators with one acidic or basic group, but if as the solution becomes more alkaline or more acid respectively, a second group begins to ionize, e.g. methyl violet, phenol phthalein, the transition range may be increased.

Since $[H'] [OH'] = k_w$

$$[H'] = \frac{k_w}{k_{In}} \cdot \frac{\alpha}{1 - \alpha} \quad (xv)$$

Since $\alpha/(1 - \alpha)$ represents the ratio of 'acid' to 'alkaline' forms, and k_w/k_{In} is a constant, the equation becomes of exactly the same type as for an indicator acid. It is quite common, therefore, to consider all indicators from the acidic point of view, it being remembered that for an indicator base the 'apparent indicator constant' is really k_w/k_{In} .

Determination of Indicator Constants—An approximate determination of the dissociation constant of an indicator may be made by finding the range of hydrogen ion concentrations in which definite colour changes are observed; * the pH of such solutions must lie within the limits of $pK_{In} \pm 1$. For more accurate results it is necessary to determine the fraction of the indicator which has changed colour in a number of solutions of known hydrogen ion concentration, and then k_{In} may be calculated by applying the standard indicator equation (x). With a one-colour indicator, e.g. phenol phthalein, the fraction of ionized (red) form can be determined by comparing the colour intensity with that of a solution containing a known amount of indicator completely transformed by the addition of a small excess of alkali; with a two-colour indicator, e.g. methyl orange, it is necessary to superimpose the acid and alkaline colours until a match is obtained.† In recent years spectro-photometric methods have been developed, by means of which it is possible to determine accurately the fraction that has changed colour of the total indicator present; such methods have been applied to the determination of indicator constants.‡

The fact that $[H'] = k_{In}$ when $\alpha = 0.5$ has also been used to determine indicator constants.§ Two solutions containing the same amount of indicator, one in the acid form and the other in the

* Friedenthal, *Z. Elektrochem.*, 1904, 10, 113; Salessky, *ibid.*, p. 204; Fels, *ibid.*, p. 208; Salm, *ibid.*, p. 344.

† McCoy, *Amer. Chem. J.*, 1904, 31, 503; Hildebrand, *Z. Elektrochem.*, 1908, 14, 349; Shugowitsch and Wegscheider, *ibid.*, p. 510; Tizard, *J. Chem. Soc.*, 1910, 97, 2477; Rosenstein, *J. Amer. Chem. Soc.*, 1912, 34, 117; Michaelis and Gyemant, *Biochem. Z.*, 1920, 109, 165; Prideaux and Nunn, *J. Chem. Soc.*, 1924, 125, 2110.

‡ Vlès, *Compt. rend.*, 1922, 175, 643; *ibid.*, 1925, 180, 584; *Bull. Soc. chim.*, 1925, 37, 558; Brode, *J. Amer. Chem. Soc.*, 1924, 46, 581; Holmes, *ibid.*, p. 627; Holmes and Snyder, *ibid.*, 1925, 47, 221, 226, 2232; Prideaux, *Chem. and Ind.*, 1926, 45, 664, 678; Sidgwick *et al.*, *Proc. Roy. Soc.*, 1930, 129 A, 537; Kortüm and von Halban, *Z. physikal. Chem.*, 1934, 170, 351; *Z. Elektrochem.*, 1934, 40, 502.

§ Salm, *Z. physikal. Chem.*, 1906, 57, 471; Clark and Lubs, *J. Bact.*, 1917, 2, 1, 109, 191.

alkaline, are superimposed; the net colour is equivalent to that of the total amount of indicator when half of it is transformed into ions ($\alpha = 0.5$). A series of solutions of known pH are then taken, the indicator is added, and the colour matched with the two superimposed solutions; the value of $[H^+]$ in the solution which agrees most closely with the colour for $\alpha = 0.5$ may be taken as k_{In} .

In some cases, e.g. *p*-nitrophenol and methyl orange, it is possible to determine the indicator constants by conductance measurements,* or by a study of the hydrolysis of the salts.† Some approximate values of indicator dissociation constants are given in Table XL (p. 264).

Determination of Hydrogen Ion Concentrations.—With **Buffer Solutions**—In the first place it is necessary to obtain, by preliminary experiments, an appropriate indicator showing a definite colour change in the particular solution under examination. The colour produced is then compared with that given by the same concentration of indicator in a series of buffer solutions of known pH ; in this way the pH of the unknown solution may be determined within 0.05 to 0.1 of a unit. Since the pH of the buffer solution is generally known, in terms of 'mean activities', from *E.M.F.* measurements (p. 367), this indicator method gives mean activities, too. In view of the uncertainty as to the exact significance of these activities, however, the results may be regarded as concentrations (cf. p. 189, footnote). For reasonable accuracy it is important that the ionic strength of the unknown solution should be the same as that of the standard buffer solution, otherwise a 'salt error' is introduced (*vide infra*).

If the pH of a coloured solution is to be determined allowance must be made for the superposition of its colour on to the indicator colour; this may be done by placing some of the test solution behind the buffer solution containing the indicator and viewing the combined colours. A simple 'comparator' for this purpose was devised by Walpole.‡ The use of dyes by means of which the buffer solution can be coloured so as to match the colour of the test solution before the addition of indicator, was suggested by Sørensen.§

In view of the general instability to light of the coloured standard buffer solutions containing an indicator it is necessary

* Bader, *Z. physikal. Chem.*, 1890, 6, 297; Hantzsch, *Ber.*, 1899, 32, 3070; Winkelblech, *Z. physikal. Chem.*, 1901, 36, 576; Hollemann, *Rec. trav. chim.*, 1902, 21, 444.

† Lundén, *J. Chim. phys.*, 1907, 5, 586.

‡ *Biochem. J.*, 1910, 5, 207; see also Biehler, *Z. physiolog. Chem.*, 1910, 110, 298; Clark and Lubs, *loc. cit.*

§ *Vide infra*.

to prepare fresh solutions at frequent intervals ; * in order to avoid this, attempts have been made to imitate the colours of various indicators at definite pH values by the use of coloured inorganic salts, e.g. ferric chloride, potassium chromate and copper sulphate.†

Without Buffer Solutions—These methods are much more approximate, but often more convenient, than the one involving buffer solutions ; they depend on the assumptions that the colour intensity of any particular indicator species is proportional to the concentration of that species, and the net colour is the sum due to ionized and non-ionized forms. If the indicator is an acid, so that the concentration of ions increases as the solution is made more alkaline, it is assumed that the addition of an excess of alkali converts the whole of the indicator into the ionized form ; free acid is assumed to make it entirely un-ionized. Hence the expression

$$[H] = k_{In} \frac{[\text{un-ionized form}]}{[\text{ionized form}]} \quad \text{. (xvi)}$$

$$\text{or} \quad pH = pk_{In} + \log \frac{[\text{ionized form}]}{[\text{un-ionized form}]} \quad \text{. (xvii)}$$

may be written :

$$pH = pk_{In} + \log \frac{\text{colour due to alkaline form}}{\text{colour due to acid form}} \quad \text{(xviii)}$$

The ratio of the two colours may be determined by matching the actual colour with the net colour obtained by superposing different thicknesses of two solutions consisting entirely of the acid and alkaline forms respectively. If the value of pk_{In} is known, the pH of the test solution can be calculated from the equation. The superposition of different amounts of the two extreme colours can be made in a number of ways.

(a) **Wedge Method** ‡—A rectangular glass box is divided into two wedge-shaped compartments by the insertion of a sheet of glass diagonally ; alternatively, two separate glass wedges may be cemented together with Canada balsam. A solution of the indicator to which a little acid has been added is placed in one wedge, and a solution with alkali in the other. By viewing the combination from the front a series of colours can be observed as a result of the superposition of gradually varying amounts of acid and alkaline colours. The test solution is placed in a glass vessel of the same thickness as the combined wedges, and indicator added so that

* Cf., Mellon and Ferner, *J. Physical Chem.*, 1931, 35, 1025 ; Kilpatrick (M.), *Chem. Reviews*, 1935, 16, 57.

† See Kolthoff, *Pharm. Weekblad*, 1922, 59, 104 ; 1923, 60, 949 ; Taub, *J. Amer. Pharm. Assoc.*, 1927, 16, 116 ; Jørgensen, *Biochem. Z.*, 1927, 186, 485 ; Mehlig and Mellon, *J. Physical Chem.*, 1931, 35, 3397.

‡ Bjerrum, *Ahren's Sammlung*, 1914, 21 ; Kolthoff, *Rec. trav. chim.*, 1924, 43, 144 ; McCrae, *Analyst*, 1926, 51, 287.

the concentration is the same as in the comparison solutions. A position is then found at which the colour of the solution matches that of the superposed acid and alkaline colours. The relative depths of the latter at this point can be measured, and the value gives the ratio of alkaline colour to acid colour in the test solution; by the use of equation (xviii) the pH of the solution may be calculated. The method is, of course, more accurate when the ratio of acid to alkaline colours is about unity, as then a small error of observation will not affect appreciably the value of the ratio.

(b) **Drop Ratio Method** *—Two series of similar tubes containing equal volumes of water are arranged in two rows so as to form n (generally 10) separate pairs; into each tube of one series is placed x drops of the acid form of an appropriate indicator, and into the corresponding tube of the other series is placed $n - x$ identical drops of the alkaline form, x varying from 0 to n along the series of tubes. Any pair of tubes, therefore, when viewed together will show a colour corresponding to a ratio of $n - x$ parts of alkaline form to x parts of acid; this quotient $(n - x)/x$ is called the 'drop ratio' for each pair of tubes. A volume of the test solution equal to that of the liquid in the tubes is placed in a similar tube and n drops of indicator added; the colour is then compared with the pairs of tubes and the 'drop ratio' corresponding to the best colour match is determined. Since

$$pH = pk_{in} + \log \frac{\text{colour of alkaline form}}{\text{colour of acid form}} \quad (\text{xviii})$$

then $pH = pk_{in} + \log \text{'drop ratio'}$; (xix)

hence the pH of the solution may be determined if the ionization constant of the indicator is known.

(c) **Colorimeter Method** †—In this method the acid form of the indicator is placed in a movable, flat-bottomed tube, surrounded by a fixed vessel containing the alkaline form; inside the inner tube is placed another, the level of which is fixed so that a constant total depth of solution is always observed when looking down the innermost tube. By moving the central tube, containing the acid form of the indicator, up and down, the ratio of the observed height of acid and alkaline solutions can be varied; the colour is then matched with that of the same total height of test solution containing the same concentration of indicator. Then

$$pH = pk_{in} + \log \frac{\text{height of alkaline solution}}{\text{height of acid solution}} \quad (\text{xx})$$

* Gillespie, *J. Amer. Chem. Soc.*, 1920, **42**, 742; Hatfield, *ibid.*, 1923, **45**, 930.

† Gillespie, *J. Bact.*, 1921, **6**, 399; Beaver, *J. Optic. Soc. Amer.*, 1929, **18**, 41.

(d) **Colorimetric Method for One-Colour Indicators**, e.g. phenol phthalein, *p*-nitrophenol.*—An accurately known amount (*t* c.c.) of a dilute indicator solution is added to the test solution so that a definite, but not too marked, depth of colour is obtained. The same indicator solution is then added gradually to a volume of alkali, e.g. *N*/100-sodium hydroxide, equal to that of the test solution, until the colour produced matches that in the solution being examined. If *a* c.c. of indicator solution are required to attain this, then in the original solution *a* c.c. of the *t* c.c. of indicator added are in the alkaline, or ionized, coloured form and *t* - *a* c.c. are in the un-ionized colourless form; hence

$$pH = pk_{In} + \log \frac{t}{t - a} \quad (xxi)$$

(e) **Spectrophotometric Methods**—For details consult the references given on page 251 in connection with the determination of indicator constants.†

Errors in Measurements with Indicator.‡—‘Acid’ Error—In all the measurements of *pH* by means of indicators an appreciable change in the hydrogen ion concentration may result from the addition of the indicator, which is an acid or base, to an unbuffered solution; § in such cases it is advisable to add a very small amount of indicator, and this should be adjusted to be near the *pH* of the test solution before addition.||

Neutral Salt Error—It has been known for some time **

* Michaelis and Gyemant, *Biochem. Z.*, 1920, 109, 165; Michaelis and Krüger, *ibid.*, 1921, 119, 307. It is assumed here that the acid form is un-ionized and colourless, but the anions are coloured; for the reverse case see Kolthoff, *J. Amer. Chem. Soc.*, 1927, 49, 1218.

† See also, Janke *et al.*, *Biochem. Z.*, 1929, 213, 154; 1932, 245, 362; Sidgwick and Woodward, *Proc. Roy. Soc.*, 1930, 130 A, 1; Russell and Latham, *Ind. Eng. Chem. (Anal.)*, 1934, 6, 463; Müller (F.), *Z. Elektrochem.*, 1934, 40, 46 (review).

‡ For review, see McCrumb and Kenny, *J. Soc. Chem. Ind.*, 1930, 49, 425 T.

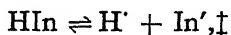
§ Fels, *loc. cit.*; Salm, *loc. cit.*

|| Cf. Pierre and Fudge, *J. Amer. Chem. Soc.*, 1928, 50, 1254; Kolthoff and Kameda, *ibid.*, 1931, 53, 525; Fawcett and Acree, *Ind. Eng. Chem. (Anal.)*, 1930, 2, 78.

** Szyzkowski, *Z. physikal. Chem.*, 1907, 58, 420; Rosenstein, *J. Amer. Chem. Soc.*, 1912, 34, 1117; Sørensen and Palitzsch, *Compt. rend. Lab. Carlsberg*, 1913, 10, 252; *Biochem. Z.*, 1913, 51, 307; Kolthoff, *Rec. trav. chim.*, 1922, 41, 54; 1923, 42, 964; 1925, 44, 275; *J. Amer. Chem. Soc.*, 1927, 49, 1218; *J. Physical Chem.*, 1928, 32, 1820; Ramage and Miller, *J. Amer. Chem. Soc.*, 1925, 47, 1230; Parsons and Douglas, *J. Bact.*, 1926, 12, 263; McBain *et al.*, *J. Gen. Physiol.*, 1926, 9, 451; 1929, 12, 695; Güntelberg and Schiodt, *Z. physikal. Chem.*, 1928, 135, 393; Sendroy and Hastings, *J. Biol. Chem.*, 1929, 82, 197; Kilpatrick (M.) and Kilpatrick (M. L.), *J. Physical Chem.*, 1930, 34, 211; Kolthoff,

that the addition of a neutral salt to a solution affects the colour of an indicator quite apart from any change due to an alteration of the hydrogen ion activity of the solution. Thus Sørensen found by *E.M.F.* measurements that the *pH*'s of solutions containing (i) 0.01*N*-hydrochloric acid alone; (ii) 0.1*N*-potassium chloride in addition; and (iii) 0.3*N*-potassium chloride in addition, were 2.01, 2.01 and 2.05 respectively, but the values determined from the colour changes of methyl violet were 2.22, 2.04 and 1.91 respectively. Since all buffer solutions used for comparison purposes contain salts, whereas the test solution may have a different salt concentration, the problem of the 'neutral salt error' is of importance. For most purposes it is desirable, if possible, to choose an indicator with a small salt error.

Two factors, at least, are operative in causing the salt effect; they are (a) the influence of the salt on the optical absorption of both forms of indicator,* and (b) the influence of the altered ionic environment on the activity of the indicator ions.† Hitherto the approximate mass action equation has been applied to the indicator equilibrium; that is probably sufficient for most purposes, as the experimental methods are approximate. For accurate determinations comparison is made with buffer solutions of known hydrogen ion activity and of definite ionic strength. The application of the exact form of the law of mass action leads, however, to interesting conclusions. Consider the indicator equilibrium in its simplest form



$$\text{then} \quad f_{\text{H}^+}[\text{H}^+] = K_{\text{In}} \frac{[\text{HIn}]}{[\text{In}']} \frac{f_{\text{HIn}}}{f_{\text{In}'}} \quad (\text{xxii})$$

where K_{In} is a true constant in all solutions of the indicator, at constant temperature. Since $-\log f_{\text{H}^+}[\text{H}^+] = \text{pH}$, and f_{HIn} may be regarded as constant,

$$\text{pH} = \text{p}K_{\text{In}} + \log [\text{In}']/[\text{HIn}] + \log f_{\text{In}'} \quad (\text{xxiii})$$

If the activity coefficient of the indicator anions may be expressed

ibid., p. 1466; Sidgwick *et al.*, *loc. cit.*; Chase and Kilpatrick (M.), *J. Amer. Chem. Soc.*, 1932, 54, 2284; Kilpatrick, *ibid.*, 1934, 56, 2048; Guggenheim and Schindler, *J. Physical Chem.*, 1934, 38, 543; Thiel and Coch, *Z. anorg. Chem.*, 1934, 217, 353; Kortüm and von Halban, *loc. cit.*

* von Halban and Ebert, *Z. physikal. Chem.*, 1924, 112, 321; Sidgwick *et al.*, *loc. cit.*

† Brønsted, *J. Chem. Soc.*, 1921, 119, 588; Clark, *The Determination of Hydrogen Ions*, 1928, p. 511.

‡ Actually HIn represents all the un-ionized forms, and In' all the ionized portions.

by the Debye-Hückel-Brønsted equation (see pp. 143, 241), it follows that

$$pH = pK_{In} + \log [In']/[HIn] - 0.5\sqrt{\mu} + C'\mu. \quad (xxiv)$$

For a given colour tint, corresponding, that is, to a definite ratio of $[In']/[HIn]$, the actual pH of the solution will depend on the value of μ , the ionic strength of the solution, and the constant C' . The value of C' will depend on the nature of the salts present; unfortunately it cannot be determined except by direct experiment on solutions of known pH . In dilute solutions ($\mu < 0.01$), the term $C'\mu$ may be neglected, and the variation of pH with ionic strength determined from the equation.

In addition to the general ionic strength effect resulting from the presence of neutral salts, some indicators are specifically affected by certain salts, e.g. phthalates precipitate methyl violet.*

The Protein Error—As a general rule indicator methods are not satisfactory for the determination of pH in solutions containing proteins. These compounds are amphoteric and colloidal in nature; hence they may combine with, as well as adsorb, indicator material, and colours may thus be obtained which are not representative of the pH of the solution. The protein error varies with the nature of the indicator and is, in general, less for simple, low molecular weight indicators than for those with complex molecules; most azo-dyes are useless in the presence of proteins, but p -nitrophenol and methyl red are only slightly affected.†

Influence of Temperature—The apparent dissociation constant of an indicator varies with the temperature, but as this constant is made up of three others (p. 248), it is impossible to foretell if it will increase or decrease with rising temperature; as a general rule, however, the constant increases as the temperature is raised.‡ A change in the dissociation constant means that the colour for a given pH will be different at a high and at a low temperature; in any case the colour absorption of the different indicator species may alter with temperature.§ For pH measurements with indicators at an elevated temperature it is necessary to use for purposes of

* Zoller and Harper, *J. Amer. Chem. Soc.*, 1921, 43, 914.

† Sørensen, *Compt. rend. Lab. Carlsberg*, 1909, 8, 1, 396; *Biochem. Z.*, 1909, 21, 131, 201, 352; *Ergeb. Physiol.*, 1912, 12, 393; Palitzsch, *Compt. rend. Lab. Carlsberg*, 1911, 10, 162; *Biochem. Z.*, 1911, 27, 131; Clark and Lubs, *loc. cit.*; St. Johnson and Peard, *Biochem. J.*, 1926, 20, 816; Lepper and Martin, *ibid.*, 1927, 21, 356; Cohen, *U.S. Public Health Rep.*, 1927, 41, 3051; Thiel and Schulz, *Z. anorg. Chem.*, 1934, 200, 225. For errors due to long-chain salts, see Hartley (G. S.) *Trans. Faraday Soc.*, 1934, 30, 444.

‡ Hastings, Sendroy and Robson, *J. Biol. Chem.*, 1925, 65, 381.

§ See Schoorl, *Chem. Weekblad*, 1906, 3, 719, 771, 807; Kolthoff, *Rec. trav. chim.*, 1921, 40, 775.

comparison, or standardization, buffer solutions in which the pH 's have been determined at that particular temperature.*

Choice of Indicators in Neutralization Titrations—In addition to the use of indicators for the direct determination of the hydrogen ion concentration, they are also employed to record the fact that a certain pH has been reached in the course of the neutralization of an acid by an alkali. It has already been seen that the pH at the acid-base equivalence point varies with the nature of the acid and the base (p. 215 *et seq.*); hence an indicator must be chosen such that its colour change occurs at the appropriate pH value.

The pH range over which an indicator changes colour has been shown to be roughly $pk_{In} - 1$ to $pk_{In} + 1$, but for purposes of neutralization titrations in volumetric analysis, it is important to know more exactly the pH at which the colour of the indicator is that generally accepted as marking the 'end-point'; this value may be called the 'titration exponent' of the indicator and given the symbol p_T . The relationship between pk_{In} and p_T depends on the nature of the indicator, and in addition on its concentration, for a one-colour indicator; the latter type will be considered first. When using a one-colour indicator, e.g. phenol phthalein, or p -nitrophenol, in a titration, the reaction is arranged so that the solution is colourless at the commencement, and the appearance of a faint colour marks the end-point. A certain minimum intensity of colour is always necessary, no matter what the total concentration of indicator; that is, a certain minimum concentration of coloured, indicator anions, $[In']_m$, is always present at the end-point. Consider two cases in which the total concentrations of the indicator are $[HIn]_a$ and $[HIn]_b$; at the end-point the concentration of anions in each case is $[In']_m$, and this is assumed to be a negligibly small fraction of the total. Let $[H']_a$ and $[H']_b$ be the hydrogen ion concentrations at the respective end-points, then using the approximate mass action treatment:

$$[H']_a = k_{In} \frac{[HIn]_a}{[In']_m} \quad . \quad . \quad (xxv)$$

and
$$[H']_b = k_{In} \frac{[HIn]_b}{[In']_m} \quad . \quad . \quad (xxvi)$$

$$\therefore \frac{[H']_a}{[H']_b} = \frac{[HIn]_a}{[HIn]_b} \quad . \quad . \quad (xxvii)$$

or
$$pH_a - pH_b = \log \frac{[HIn]_b}{[HIn]_a} \quad . \quad (xxviii)$$

* For references, see p. 242 *supra*.

The pH at the end-point marked by a one-colour acid indicator is, therefore, lower the greater the total indicator concentration; the titration exponent for these indicators depends on the concentration. Working with phenol phthalein ($pK_{in} = 9.7$) Koltzoff* has found that a concentration of 2×10^{-6} gm. ions per litre of coloured anions is required to yield the rose colour marking the usual end-point; the concentration of a saturated aqueous solution of this indicator is 2.5×10^{-4} gm. mols. per litre; hence p_T for such a solution is given by the expression

$$p_T = p_{k_{in}} + \log \frac{[In']_m}{[HI n]} \quad (xxix)$$

$$= 9.7 + \log \frac{2 \times 10^{-8}}{2.5 \times 10^{-4}} = 7.6.$$

In an ordinary titration using, say, 0.1 c.c. of a 1 per cent. (alcoholic) solution of phenol phthalein to 100 c.c. of titrated solution, the indicator exponent may be calculated as 8.5, assuming that $[In']_m$ has the same value as found by Kolthoff. The *fraction* of indicator in the form of ions at the end-point clearly varies with the concentration, but according to Noyes† when using the smallest reasonable amount of indicator a conversion of 25 per cent. is necessary to produce a visible colour. Under these conditions $[In']/[HIn]$ is 1/3, hence

$$p_T = pk_{In} + \log \frac{1}{3}$$
$$= pk_{In} - 0\cdot5 \quad . \quad . \quad . \quad (\text{xxx})$$

This represents the highest practicable value for p_T , and the smallest value depends on the solubility of the indicator; in general, however, the indicator concentration is such as to give a value of p_T approximately equal to $pk_{In} - 1$.

Two-Colour Indicators—With a two-colour indicator it is usual to titrate to a certain colour *tint* rather than intensity; this tint corresponds to a definite ratio of ionized to un-ionized forms irrespective of the total indicator concentration. The titration exponent is thus independent of the amount of indicator added. The extent of ionization at the accepted end-point depends on the direction in which the titration is carried out; thus Noyes found that methyl orange showed a colour change in going from yellow to red when 5 to 20 per cent. of the indicator was in the red form, but in going from red to yellow a 20 to 30 per cent. conversion was necessary before a definite colour change could be observed. As a general rule two-colour indicators are used in such a way that at the end-point the colour changes from the lighter to the darker

* Kolthoff and Furman, *Indicators*, 1926, p. 81.

† *J. Amer. Chem. Soc.*, 1910, 32, 815.

colour, e.g. yellow to red with methyl orange; in this direction a 10 per cent. conversion may be regarded as an average value. The titration exponent is, therefore, equal to $pk_{\text{In}} + 1$, or $pk_{\text{In}} - 1$, according to whether the lighter coloured form is alkaline or acid, respectively. If titration has to be carried out in the reverse direction, i.e. from dark to lighter colour, then a 25 per cent. conversion is necessary and the pH at the end-point is equal to $pk_{\text{In}} + 0.5$, if the alkaline form is the darker, or $pk_{\text{In}} - 0.5$ if it has the lighter colour.

Apart from its influence on the titration exponent, too large a concentration of indicator is not advisable; in the first place, it adds a certain amount of acid or alkali to the solution being titrated. This error may be avoided by adding the indicator in the form it has at the end-point. In the second place, the change of colour is often more difficult to detect in an intensely coloured solution, and dichroism, i.e. a variation in colour *tint*, apart from intensity, for different thicknesses, further complicates the situation. In Table XXXIX (p. 261) are given some approximate titration exponents for a number of useful indicators.*

Colour Change in Titrations—Since the pH at the equivalence point can be calculated from a knowledge of the dissociation constants of the acid and base being titrated against one another, it should be possible to choose an indicator with the correct titration exponent. The accuracy of the results obtained will depend, however, on another factor, namely a sharp end-point; that is, the addition of one drop (0.03 to 0.05 c.c.) of titrant should produce a definite colour change at the end-point. In other words, in the vicinity of the equivalence point one drop of acid or alkali should cause a very marked change in the pH of the solution. This condition is satisfied if the pH -neutralization curve shows a marked inflexion, and hence depends on the dissociation constants and concentrations of the acid and alkali being titrated. Noyes † has calculated that when a 0.1N-solution of a weak acid is titrated with a strong base the theoretical accuracy attainable is 0.1, 0.33 and 1.0 per cent. if the dissociation constants are not smaller than 10^{-6} , 10^{-7} and 10^{-8} respectively; the same holds for a weak base and strong acid. If both acid and base are weak the limits of accuracy correspond to values of $k_a \times k_b$ equal to 10^{-6} , 10^{-7} and 10^{-8} respectively.

From the pH -neutralization curves (Figs. 13-16) it may be concluded that a strong acid and strong base should always give a sharp end-point; a medium weak acid, e.g. acetic acid, will give

* Taken from Kolthoff and Furman, *op. cit.*, p. 109; compare the values for pT with the figures quoted in Table XL, p. 264 *infra*.

† *loc. cit.*

TABLE XXXIX
TITRATION EXPONENTS OF SOME USEFUL INDICATORS

Indicator.	p _r .	End-Point Colour.	Concentration.
Thymol blue . .	2.6	Yellowish-rose	1 c.c. 1% sol. per 100 c.c.
Bromphenol blue .	4	Purplish-green	0.5-1 c.c. 1% sol. per 100 c.c.
Methyl orange .	4	Orange	0.2-0.5 c.c. 1% sol. per 100 c.c.
Methyl red . .	5	Yellowish-red	0.2-0.5 c.c. 2% sol. per 100 c.c.
Bromcresol purple	6	Purplish-green	0.5-1.0 c.c. 1% sol. per 100 c.c.
Bromthymol blue .	6.8	Green	0.5-1.0 c.c. 1% sol. per 100 c.c.
Phenol red . .	7.5	Rose-red	0.5-1.0 c.c. 1% sol. per 100 c.c.
Cresol red . . .	8	Red	0.5-1.0 c.c. 1% sol. per 100 c.c.
Thymol blue (second range)	8.8	Blue-violet	0.5-1.0 c.c. 1% sol. per 100 c.c.
Phenol phthalein .	9	Pale rose	0.3-0.4 c.c. 1% sol. per 100 c.c.

a fairly good end-point if titrated with a strong base, and similarly a weak base may be titrated with a strong acid. If a weak base is titrated with a weak acid, or if a very weak base (or acid) is titrated with any acid (or base), especially in dilute solutions, the end-point cannot be sharp. In these cases it is possible to carry out the titration in an approximate manner only by the use of a comparison solution, known to contain equivalent amounts of the acid and base being titrated, and the same concentration of indicator as in the titrated solution. When the colour tint in the test solution is the same as in the comparison solution it may be assumed that the equivalence point is reached in the titration; the accuracy of this method is limited by the ability of the eye to match colours. By the use of artificial means of colour comparison more accurate results may be obtained.

In a displacement reaction, e.g. sodium acetate by hydrochloric acid, which is equivalent to the neutralization of a very weak acid (p. 227), the inflexion at the equivalence point is not marked; hence indicator methods are of no use in aqueous solution unless the salt of a very weak acid, e.g. a carbonate or borate, is being titrated. It has been already seen that in an alcoholic medium the inflexion in the pH curve at the equivalence point is much more

marked and a number of displacement titrations have been carried out in ethyl alcohol solution with the aid of indicators. Under these conditions sharp colour changes can be observed, whereas in aqueous solution they are gradual.*

In the titration of a mixture of acids the inflexion at the first equivalence point depends on the ratio $c_I k_I / c_{II} k_{II}$, where c_I and c_{II} are the concentrations, and k_I and k_{II} the dissociation constants of the stronger and weaker acid, respectively. Noyes has shown that this ratio must be not less than 10^7 , 10^6 and 10^5 for an accuracy of 0.1, 0.33 and 1.0 per cent. respectively.† The accuracy for the titration of the total acid, like the final point of inflexion, depends only on the value of k_{II} and the concentration of the solution. The sharpness of the end-point in the neutralization of a mixture of a mineral acid and an organic acid of moderate strength may be improved by working in 90 per cent. acetone solution. The strength of the strong acid is hardly affected, but the dissociation constant of the weaker is greatly diminished (cf. p. 227). The final end-point under these conditions will be vague.‡ For a dibasic acid the conditions are similar to those in a mixture of equivalent amounts of two monobasic acids; hence k_1/k_2 must not be less than 10^7 , 10^6 or 10^5 , for an accuracy of 0.1, 0.33 or 1.0 per cent. respectively, in the determination of the *first* equivalence point. The final end-point depends on the value of k_2 . Exactly similar conclusions are applicable to mixtures of bases and to di-acid bases.§

Choice of Indicators—The less marked the inflexion in the pH-neutralization curve the more restricted is the choice of indicators. In the titration of 0.1*N* strong acid with 0.1*N* strong base (Fig. 13), although the exact equivalence point occurs at pH 7, the pH of the solution changes from 4 to 10 between 0.1 per cent. excess of acid and 0.1 per cent. excess of base. Any indicator changing colour between pH 4 and 10 can thus be used to give a titration result within 0.1 per cent. of the theoretical value, apart from experimental errors. If the solutions are diluted to 0.01*N*, the pH limits for an accuracy of 0.1 per cent. are reduced to 5–9, and consequently methyl orange ($p_T = 4.0$) will give results at least

* Bishop, Kittredge and Hildebrand, *J. Amer. Chem. Soc.*, 1922, **44**, 135; Kolthoff, *J. Physical Chem.*, 1931, **35**, 2732. It should be noted that the indicator constant will probably be different in alcoholic and aqueous solutions (cf. Thiel and Greig, *Z. physikal. Chem.*, 1935, **172**, 245), and so also will be the pH at the end-point.

† See also Tizard and Boeree, *J. Chem. Soc.*, 1922, 121, 132; Kolthoff and Furman, *op. cit.*, p. 121 *et seq.*

‡ Richardson, *Proc. Roy. Soc.*, 1934, **115 B**, 170.

§ For further discussion of titrations see Kolthoff and Furman, *op. cit.*; Prideaux, *The Theory and Use of Indicators*; Smith, *Analytical Processes*.

1 per cent. in error. With still more dilute solutions the choice of indicator is limited further. When 0.1*N*-acetic acid is titrated with 0.1*N*-sodium hydroxide the *pH* at the equivalence point is 8.87, and the limits for an error of 0.1 per cent. are 7.8 to 10; of the common indicators, phenol phthalein ($p_T = 9$) is the most suitable, but the choice is very restricted. When the inflexion at the equivalence point is less marked, e.g. with ammonia and acetic acid, only one indicator is generally available, and even then a comparison solution must be used.

Useful Indicators—From the discussion of the theory of neutralization and the theory of indicators given here it should be possible to determine beforehand the most suitable indicator for any particular titration, and also to know if the end-point will be reasonably sharp. A range of indicators is desirable both for titration purposes and for the determination of *pH*'s; although many have been suggested, few are satisfactory* for most purposes. A good indicator should be stable, have small salt and protein errors, show a distinct colour change over a small range of *pH*, and the colours should be brilliant. The first selection of indicators was made by Sørensen † from those known at the time; later Clark and Lubs ‡ introduced the use of a group of sulphonephthaleins, and Michaelis § compiled a list of one-colour indicators. In Table XL (on page 264) is given a range of indicators suggested by Clark || based on the original selection of Clark and Lubs, supplemented by those of Cohen.** These indicators are neutralized with sodium hydroxide and used in 0.04 per cent. solution.

Multiple Range Indicators—Certain substances have more than one ionizable group associated with a tautomeric change involving a colour change; such substances can act as indicators over two or more ranges of *pH*, the values depending on the constants for the respective groups. In Table XL both meta-cresol purple and thymol blue appear twice; each has two distinct ranges, corresponding with the ionization of different groups, over which it serves as a useful indicator. One of the earliest investigations of this type of substance was made by Henderson and

* Clark, *International Critical Tables*, Vol. I, 1926, p. 84, lists over 200 indicators. See also Kolthoff, *Säure-Basen Indicatoren*, 1932.

† *Compt. rend. Lab. Carlsberg*, 1909, 8, 1; *Biochem. Z.*, 1909, 21, 131, 201.

‡ *J. Bact.*, 1917, 2, 1, 109, 191.

§ *Biochem. Z.*, 1920, 109, 165; 1921, 119, 307.

|| *The Determination of Hydrogen Ions*, 1928, p. 94.

** *U.S. Public Health Rep.*, 1927, 41, 3051; see also McCrumb and Kenny, *Ind. Eng. Chem. (Anal.)*, 1929, 1, 44. It may be noted that 'nitrazine yellow' has been proposed as an indicator giving a sharp colour change between *pH* 6.4 and 6.8 (Wenker, *Ind. Eng. Chem.*, 1934, 26, 350).

TABLE XL
INDICATORS RECOMMENDED BY CLARK

Indicator.	pK_{in}	pH Range.	Acid.	Colour Change : Alkaline.	Chemical Name.
Meta-cresol purple.	1.51	1.2-2.8	Red	Yellow	<i>m</i> -cresol sulphone-phthalein.
Thymol blue . .	1.51	1.2-2.8	Red	Yellow	thymol sulphone-phthalein.
Bromphenol blue .	3.98	3.0-4.6	Yellow	Blue	tetrabromophenol sulphone-phthalein.
Bromcresol green .	4.67	3.8-5.4	Yellow	Blue	tetrabromo- <i>m</i> -cresol sulphone-phthalein.
Chlorphenol red .	5.98	4.8-6.4	Yellow	Red	dichlorophenol sulphone-phthalein.
Bromphenol red .	6.16	5.2-6.8	Yellow	Red	dibromophenol sulphone-phthalein.
Bromcresol purple.	6.3	5.2-6.8	Yellow	Purple	dibromo- <i>o</i> -cresol sulphone-phthalein.
Bromthymol blue .	7.0	6.0-7.6	Yellow	Blue	dibromothymol sulphone-phthalein.
Phenol red . . .	7.9	6.8-8.4	Yellow	Red	phenol sulphone-phthalein.
Cresol red . . .	8.3	7.2-8.8	Yellow	Red	<i>o</i> -cresol sulphone-phthalein.
Meta-cresol purple	8.32	7.4-9.0	Yellow	Purple	<i>m</i> -cresol sulphone-phthalein.
Thymol blue . .	8.9	8.0-9.6	Yellow	Blue	thymol sulphone-phthalein.
Cresol phthalein .	9.4	8.2-9.8	Colourless	Red	<i>o</i> -cresolphthalein.
<i>Other Indicators.</i>					
Methyl orange (0.01%)	3.7	3.1-4.4	Red	Yellow	<i>p</i> -benzene sulphonic acid-azodimethyl aniline.
Methyl red (0.02%)	5.1	4.2-6.3	Red	Yellow	<i>o</i> -carboxybenzene-azo-dimethylaniline
<i>p</i> -Nitrophenol (0.04%)	7.1	5.6-7.6	Colourless	Yellow	<i>p</i> -nitrophenol.
Phenolphthalein (0.05%)	9.4	8.3-10.0	Colourless	Red	phenolphthalein.

Forbes; * these authors found that 2:5-dinitro-hydroquinone exhibited the following colours:

pH	2	4	6	8	10	12
Colour:	green-yellow	orange	orange	brown-red	red-purple	purple

Such a substance could be used to give a rough indication of the pH of a solution from 2 to 12. Mixed indicators have been applied for the same purpose, and by means of a single indicator solution it is possible to determine the pH of an electrolyte, over a wide range, within 0.5 unit.†

* *J. Amer. Chem. Soc.*, 1910, 32, 687.

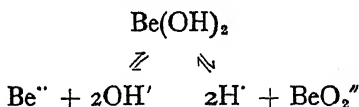
† See Kolthoff, *Biochem. Z.*, 1927, 189, 26; *Pharm. Weekblad*, 1929, 66, 67; van Urk, *ibid.*, 1928, 65, 1246; Fairbrother, *Industrial Chemist*, 1928, 4, 93; Pieters, *Chem. Weekblad*, 1935, 32, 539; Clark, *op. cit.*, p. 97; Britton, *op. cit.*, p. 286.

[For use of indicators in non-aqueous solutions, see Cray and Westrip, *Trans. Faraday Soc.*, 1925, 21, 326 (acetone); Conant and Hall (N. F.), *J. Amer. Chem. Soc.*, 1927, 49, 3062; Hammett and Deyrup, *ibid.*, 1932, 54, 2721 (acetic acid); *Idem.*, *ibid.*, p. 4239 (formic acid); Kolthoff, *J. Physical Chem.*, 1931, 35, 2732 (alcohol); Brønsted, *Ber.*, 1928, 61, 2049; La Mer and Downes, *J. Amer. Chem. Soc.*, 1933, 55, 1840 (benzene); Kilpatrick (M.) and Kilpatrick (M. L.), *Chem. Reviews*, 1933, 13, 131 (acetonitrile); Müller (A.), *Z. anorg. Chem.*, 1934, 217, 113; 218, 210 (chloroacetic acids)].

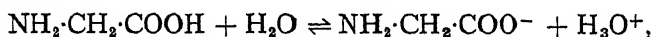
CHAPTER XI

THE THEORY OF AMPHOTERIC ELECTROLYTES

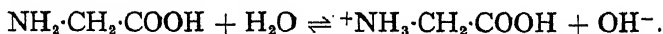
AMPHOTERIC Electrolytes—An amphoteric substance, or ampholyte, is one which can react either as an acid or as a base; that is, it can, according to circumstances, either supply or take up protons. A number of feebly basic inorganic hydroxides, e.g. $\text{Be}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, $\text{Pb}(\text{OH})_2$, $\text{Sn}(\text{OH})_2$, $\text{As}(\text{OH})_3$, are able to form salts either with acids or with bases, and hence are termed amphoteric. In solution these compounds presumably ionize in two ways, e.g.



In the presence of acids the hydroxyl ions are removed and further basic ionization occurs, whereas the presence of alkali favours the acidic dissociation. It is to be noted that in the amphoteric hydroxides it is the same group, viz. OH , which is capable of acting in two ways. Organic ampholytes are somewhat different in their fundamental nature, as these substances contain at least two separate groups, one of which has acidic and the other basic functions.* For example, glycine (i.e. amino-acetic acid) or any other amino-acid, has a $-\text{COOH}$ group and an $-\text{NH}_2$ group; the former can presumably yield a proton and the latter accept a proton in aqueous solution. The acidic ionization would be represented as



and the basic ionization would be



In the presence of acids the basic ionization is favoured and the acidic depressed; hence glycine will act as a base. In alkaline solution, however, the acidic ionization occurs almost exclusively

* See Ostwald, *Z. Elektrochem.*, 1899, 6, 36.

$$\text{From equation (iii)} \quad [A^-] = k_a \frac{[A]}{[H^+]} \quad . \quad (\text{vi})$$

$$\text{and from equation (iv)} \quad [A^+] = k_b \frac{[A]}{[OH^-]} \quad . \quad (\text{vii})$$

Substituting in equation (v),

$$[H^+] + k_b \frac{[A]}{[OH^-]} = k_a \frac{[A]}{[H^+]} + [OH^-] \quad . \quad (\text{viii})$$

$$\text{Since} \quad [OH^-] = k_w/[H^+]$$

$$[H^+] + \frac{k_b}{k_w} [H^+] [A] = k_a \frac{[A]}{[H^+]} + \frac{k_w}{[H^+]} \quad . \quad (\text{ix})$$

$$[H^+]^2 \left\{ 1 + \frac{k_b}{k_w} [A] \right\} = k_a [A] + k_w$$

$$[H^+] = \sqrt{\frac{k_a [A] + k_w}{k_b [A]/k_w + 1}} \quad . \quad . \quad . \quad (\text{x})$$

This equation connects the hydrogen ion concentration of a pure ampholyte with the ionization constants and the total concentration of un-ionized molecules; as the latter cannot be determined directly the calculation of $[H^+]$ can only be made by a process of approximation (*vide infra*). Sørensen* has eliminated the term $[A]$ from equation (ix), but the resulting form involves the fourth power of $[H^+]$ and a direct solution is difficult. It is simpler, therefore, to adopt the following method of applying equation (x).† In the first place $[A]$ is taken as equal to the total concentration of ampholyte, c , and an approximate value of $[H^+]$ is calculated. Thus, for a 0.01*N*-solution of *m*-amino-benzoic acid $k_a = 1.6 \times 10^{-5}$, $k_b = 1.2 \times 10^{-12}$ and c is 0.01; from equation (x), and taking k_w to be 10^{-14} , the value of $[H^+]$ is found to be roughly 2.7×10^{-4} . With this value for $[H^+]$ and still taking $[A] = c$, approximate values for $[A^+]$ and $[A^-]$ may be obtained by substitution in equations (iii) and (iv); in the present case these are found to be 3.2×10^{-4} and 6×10^{-4} respectively. The total amount of ampholyte (c) is made up of the un-ionized portion and the two types of ions A^+ and A^- , hence

$$c = [A] + [A^+] + [A^-] \quad . \quad . \quad . \quad (\text{xi})$$

From the approximate values of $[A^+]$ and $[A^-]$ a value of $[A]$ may be calculated as 0.908×10^{-2} , and on substituting in equation (x) a more accurate value for $[H^+]$ is determined as 2.5×10^{-4} . The calculation may, if desired, be repeated in order to obtain a still

* *Ergebn. d. Physiol.*, 1912, 12, 495; see Michaelis, *Hydrogen Ion Concentration*, Eng. trans., 1926, p. 74.

† Walker, *loc. cit.*; Kolthoff and Furman, *Indicators*, 1926, p. 42.

more exact value; this is, however, rarely necessary. A more precise evaluation of $[A^+]$ and $[A^-]$ can now be made with the final value of $[H^+]$.

Equation (x) may be written in the form

$$[H^+] = \sqrt{k_w \frac{k_a[A] + k_w}{k_b[A] + k_w}}, \quad \dots \quad (xa)$$

hence if $k_a > k_b$, as is generally the case, $[H^+] > \sqrt{k_w}$, i.e. $[H^+] > 10^{-7}$, and the solution of the pure ampholyte is acid; but if $k_a < k_b$ the solution would be alkaline. In the special case when $k_a = k_b$, $[H^+]$ is always equal to $\sqrt{k_w}$, independent of the concentration of the ampholyte, and the solution is neutral. Further, under these conditions, it follows from equations (iii) and (iv) that

$$\frac{[A^+]}{[A]} = \frac{[A^-]}{[A]} = \text{a constant, independent of dilution.}$$

Hence

$$\frac{[A^+] + [A^-]}{[A]} = \frac{\text{Ionized portion of ampholyte}}{\text{Un-ionized portion of ampholyte}} = \text{a constant.}$$

The total degree of ionization of the ampholyte in which $k_a = k_b$ is thus independent of dilution, and the equivalent conductance is a constant. This result shows clearly that conductance relationships of ampholytes are quite different from those of simple electrolytes.

In general the total conductance of an ampholyte is the sum of the conductances of at least four ions, viz. H^+ , OH^- , A^+ and A^- ; hence any attempt to determine the degree of dissociation from the conductance ratio, or to calculate a 'dissociation constant' from such results is doomed to failure.* The apparent equivalent conductance of the ampholyte is the sum of the products of the concentrations of the ions and their respective ion conductances at the particular dilution of the solution, thus

$$\Lambda = \Lambda_{H^+}[H^+] + \Lambda_{OH^-}[OH^-] + \Lambda_{A^+}[A^+] + \Lambda_{A^-}[A^-]. \quad (xii)$$

Although this relationship is not applicable directly to the calculation of a dissociation constant, it will be shown later how it may be used indirectly to determine the constant for the stronger function of the ampholyte.

Iso-electric Point of an Ampholyte—An ampholyte is at its iso-electric point when the extent of its ionization as an acid is equal to that as a base; that is when $[A^+] = [A^-]$. If both $[A^+]$ and $[A^-]$ are large ions they will have almost the same speeds,

* Cf. Ostwald, *Z. physikal. Chem.*, 1889, 3, 261; Winkelblech, *ibid.*, 1901, 36, 546.

and so under the influence of an electric current equal amounts will migrate in opposite directions; at the iso-electric point, therefore, a complex ampholyte appears to remain stationary in an electric field.

From equations (iii) and (iv) it follows that

$$\frac{[A^-]}{[A]} = \frac{k_a}{[H^+]} \text{ and } \frac{[A^+]}{[A]} = \frac{k_b}{[OH^-]} \quad (\text{xiii})$$

Hence at the iso-electric point, when $[A^+] = [A^-]$,

$$\frac{k_a}{[H^+]} = \frac{k_b}{[OH^-]} = \frac{k_b[H^+]}{k_u}$$

$$[H^+] = \sqrt{\frac{k_a k_u}{k_b}} \quad (\text{xiv})$$

By means of this equation it is possible to calculate the hydrogen ion concentration of an ampholyte at its iso-electric point.*

It should be made clear that in general it is not possible to obtain an iso-electric solution of a *pure* ampholyte, since equation (xa) for a pure amphoteric substance can only become identical with equation (xiv) for the iso-electric point when $k_a = k_b$, or when $[A]$ is infinite. If k_a is not equal to k_b , the hydrogen ion concentration of the ampholyte approaches the value at the iso-electric point as the total concentration is increased, but the actual value can never be attained. It is usual to add a small amount of alkali or acid in order to obtain an iso-electric solution of an amino-acid, or other ampholyte. When the hydrogen ion concentration of an ampholyte is made greater than the value at the iso-electric point the acidic ionization becomes smaller than the basic, and the solution behaves as a base; on the other hand, if the hydrogen ion concentration is brought below the iso-electric value the basic properties of the ampholyte exceed the acidic. Michaelis † has used these facts in order to determine the iso-electric points of amino-acids. A definite amount of ampholyte is added to each of a series of buffer solutions and the change in pH observed; if the ampholyte causes an increase of pH it is acting as a base, and the hydrogen ion concentration of the buffer is below that of the iso-electric point. If the ampholyte lowers the pH then its iso-electric point is at a greater hydrogen ion concentration than in the buffer. When the addition of amino-acid causes no change in the pH of the buffer then the latter has the same hydrogen ion concentration as the iso-electric ampholyte.

* Michaelis and Mostynski, *Biochem. Z.*, 1910, 24, 79; Hahn and Klockmann, *Z. physikal. Chem.*, 1931, 157, 209.

† *Biochem. Z.*, 1913, 47, 251.

It has been stated that

$$c = [A] + [A^+] + [A^-] \quad \dots \quad (xi)$$

where c is the total concentration of ampholyte. Substituting values for $[A^+]$ and $[A^-]$ obtained from equations (iii) and (iv), and dividing through by $[A]$ it is found that

$$\frac{c}{[A]} = 1 + \frac{k_a}{[H^+]} + \frac{k_b}{k_w} [H^+] \quad (xv)$$

and differentiating with respect to $[H^+]$ it follows that

$$\frac{d\left(\frac{c}{[A]}\right)}{d[H^+]} = -\frac{k_a}{[H^+]^2} + \frac{k_b}{k_w} \quad \dots \quad (xvi)$$

The quantity $c/[A]$ is a minimum, and so $[A]$ a maximum, when this differential coefficient is equal to zero; that is when

$$\frac{k_a}{[H^+]^2} + \frac{k_b}{k_w} = 0$$

or

$$[H^+] = \sqrt{\frac{k_a k_w}{k_b}} \quad (xvii)$$

This is the hydrogen ion concentration at the iso-electric point; hence in this state the concentration of un-ionized ampholyte,* $[A]$, is a maximum, and the degree of ionization is a minimum. Since the physical properties, e.g. solubility, viscosity, etc., of the un-ionized form probably differ from those of the ionized forms it is natural to suppose that maxima or minima will be found at the iso-electric point. This is actually found to be the case in many instances, and Michaelis and Davidsohn† have based an approximate method for the determination of the iso-electric point on the fact that sparingly soluble ampholytes have a minimum solubility at this point.

Neutralization of Amino-Acids—In general an amino-acid may be regarded as made up of an acid and a base which are independent of one another; if a strong acid is added the basic function of the ampholyte predominates, and as a consequence of this addition of hydrogen ions the acidic function becomes negligible. Similarly if a strong base is added the acidic function of the amino-acid operates almost exclusively. If the acidic and basic dissociation constants of the ampholyte are known, the separate pH-neutraliza-

* According to modern views the so-called 'un-ionized' form of many amino-acids is actually a 'dual ion' (p.277). It carries both a positive and a negative charge and so is electrically neutral, although it has a large dipole moment.

† *Ibid.*, 1910, 30, 140.

tion curves can be determined by the use of approximate equations; these are derived from the Henderson-Hasselbalch equation and take the forms:

$$pH = pk_a + \log [\text{salt}]/[\text{un-neutralized ampholyte}] \quad (\text{xviii})$$

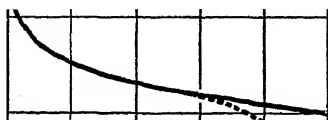
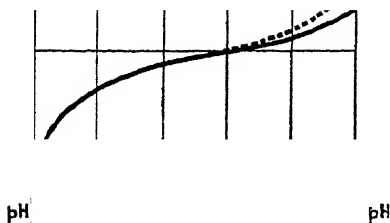
for the neutralization of the acid function, and

$$\begin{aligned} pH &= pk_w - pOH \\ &= pk_w - pk_b - \log [\text{salt}]/[\text{un-neutralized ampholyte}] \quad (\text{xix}) \end{aligned}$$

for the basic ionization. These formulæ are not applicable at the

Per Cent. Acidic function Neutralized

40 60 80



Per Cent. Basic function Neutralized

FIG. 18.—Acidic and basic titration curves of glycine

beginning and end of the neutralization (p. 219); the pH at the equivalence points may be calculated by the methods used for single weak acids or weak bases, provided the concentration of the solution is known. The pH of the original ampholyte solution may be evaluated by the method already described (p. 268). The curves shown in Fig. 18 have been calculated for 0.1*N*-amino-acetic acid, on the basis of the values $pk_a = 9.7$, and $pk_b = 11.5$;* neither for the acidic nor for the basic function is there a sharp inflexion at the equivalence point.† This absence of inflexion may be related to the fact that the buffering power of water is appreciable at pH's less than 3 and greater than 11 (p. 244). Had there been no buffering the curves would have followed the dotted lines in Fig. 18, the pH values at the equivalence point being taken as $pk_a + 2$ for the acid, and $pk_b - 2$ for the base, since at these values the respective forms should be 99 per cent. neutralized (cf. p. 231). In the case under discussion the two neutralization curves are well separated; it is clear, therefore, that the basic function does not

* See Tague, *J. Amer. Chem. Soc.*, 1920, **42**, 173; Harris, *loc. cit.*; *J. Chem. Soc.*, 1923, **123**, 3294; Branch and Miyamoto, *J. Amer. Chem. Soc.*, 1930, **52**, 863, for experimental curves.

† The absence of a marked inflexion accounts for the use of glycine in buffer solutions, see p. 242.

operate appreciably, whilst the acid is being neutralized, and vice versa. It has been shown (p. 230) that the neutralization of an acid may be regarded as commencing—actually 1 per cent.—at $pH = pk_a - 2$, and of a base at $pH = pk_w - pk_b + 2$; hence if the neutralization curves for an ampholyte are to be distinct $pk_a - 2$ must be greater than $pk_w - pk_b + 2$, i.e. $pk_a + pk_b$ must be greater than $pk_w + 4 = 18$; in other words $k_a \times k_b < 10^{-18}$ for the curves to be separate. For glycine $pk_a + pk_b$ is 21.2, so the two curves are distinct. With *p*-amino-benzoic acid, however, pk_a is 5.2 and pk_b 11.6, then $pk_a + pk_b$ is 16.8, and the *theoretical* neutralization curves are not separate, but cross one another. The pH 's in the early stages of neutralization of each function are thus affected by the ionization of the other; after about 10 per cent. of neutralization of either form, the ionization of the other form is almost completely suppressed in this particular case. The smaller the value of $pk_a + pk_b$ the more pronounced is the effect of the opposite function of the ampholyte. Incidentally it may be shown that the pH at which the two hypothetical neutralization curves cross is that of the iso-electric point, since the total concentration of positive and negative ions is then a minimum.*

Titration of Amino-Acids—Since the pH -neutralization curves show no inflexion at the equivalence point it would appear that quantitative titrations of amino-acids could not be carried out; the allowance necessary to compensate for the buffer action of water can, however, be determined and 'corrected' curves, identical with the dotted portions of Fig. 18, having sharp inflexions, may be obtained.† By adding known amounts of strong acid, or base, to a volume of water equal to that of the titrated solution of amino-acid, until the same pH is reached as in the various stages of titration, the amount of *free* strong acid, or base, at those stages can be determined.‡ By subtracting this amount from the total amount of acid, or base, added in the titration, the quantity actually *used up* in neutralizing the basic, or acidic function, respectively, of the ampholyte is determined. The values so obtained when plotted against the corresponding pH 's give curves in which the effect of hydrolysis and buffer action is eliminated, and hence show definite inflexions. By measuring the pH 's electrometrically (p. 385) the method described can be used for the accurate estimation of amino-acids.

* As already noted, p. 271 footnote, the concentration of *dual* ions may be a maximum.

† Tague, *loc. cit.*; Harris, *loc. cit.*

‡ The assumption is made that the pH of the titrated solution is due entirely to the free strong acid, or base, and not at all to the ampholyte; this will be true in the vicinity of the equivalence point.

Determination of Apparent Dissociation Constants.—

Hydrogen Ion Method—When either function of an amino-acid is half-neutralized, then provided the other function does not interfere, the pH of the solution will be equal to pk_a for the neutralization of the acidic function, or to $pk_w - pk_b$ if the basic portion is being neutralized. The method is similar to that available for a single weak acid or weak base. It is essential, however, that hydrolysis should be inappreciable at the half-neutralization point; this is almost invariably the case. One equivalent of amino-acid may be mixed with one-half equivalent of strong acid, or strong base, and the pH of the resulting solution determined by *E.M.F.* (p. 385) or indicator methods. If the equivalent weight or concentration of the acid is unknown, use may be made of the 'corrected' titration curves; the values of pk_a or pk_b may be found from various points of this curve by means of the appropriate form of the Henderson equation, or from the pH value at the half-neutralization point only.* If either k_a or k_b is known the other constant can be determined by applying equation (x), together with the value for $[H^+]$, measured by *E.M.F.* or by indicators, in a solution of pure ampholyte of known concentration. An approximation method, such as that described on page 268 would have to be used.

Hydrolysis Method—If the basic dissociation constant of an amino-acid is very small, the sodium salt of the acid will behave, as regards hydrolysis, like the salt of a simple acid; in the same way the hydrolysis of the hydrochloride of an amino-acid will be comparable with that of any hydrochloride of a weak base, provided the acidic dissociation constant is small.† The hydrolysis constant of the sodium salt, or of the hydrochloride, may be determined and the dissociation constant of the acidic, or basic, function calculated by the usual equations: $k_a = k_w/k_b$, or $k_b = k_w/k_a$, respectively. The hydrolysis may be studied by any of the methods already described (Chap. VIII); the reaction velocity and conductance methods have been chiefly used.‡

Solubility Method—This is really an approximate form of the hydrolysis method, applicable when the dissociation constant is very small and hence hydrolysis considerable; the free ampholyte must be sparingly soluble in water for the method to be of any

* Harris, *loc. cit.*; Branch and Miyamoto, *loc. cit.*; Ogston and Brown (J. F.), *Trans. Faraday Soc.*, 1935, 31, 574; see also, Harned and Owen, *J. Amer. Chem. Soc.*, 1930, 52, 5091; Owen, *ibid.*, 1934, 56, 24.

† See Lundén, *J. Biol. Chem.*, 1908, 4, 267.

‡ Winkelblech, *Z. physikal. Chem.*, 1901, 36, 546; Lundén, *ibid.*, 1906, 54, 532; Johnston (H.), *Proc. Roy. Soc.*, 1906, 78, A, 82; Cumming, *ibid.*, p. 103; Kanitz, *Z. physiol. Chem.*, 1906, 47, 476; Zawidski, *Ber.*, 1903, 36, 3325; 1904, 37, 153, 2289; Holmberg, *Z. physikal. Chem.*, 1908, 62, 726.

value. If c_o gm. equiv. per litre is the solubility of the ampholyte in water, and c_b the solubility in a solution containing b gm. equiv. per litre of a strong base, then in the alkaline solution c_o may be regarded as the concentration of un-ionized ampholyte, $[A]$, and $c_b - c_o$ the concentration of negative ampholyte ions ($[A^-]$). The amount of free, un-neutralized alkali in the solution is $b - (c_b - c_o)$ gm. equiv. per litre, and if this may be regarded as completely ionized, then $[OH']$ is equal to $b - (c_b - c_o)$. Hence

$$k_a = \frac{[H'] [A^-]}{[A]} = \frac{[A^-]}{[A]} \cdot \frac{k_w}{[OH']} = \frac{c_b - c_o}{c_o(b - c_b + c_o)} k_w \quad (xx)$$

Similarly if c_a is the solubility of the ampholyte in a solution containing a gm. equiv. of a strong acid per litre, then

$$k_b = \frac{[OH'] [A^+]}{[A]} = \frac{[A^+]}{[A]} \cdot \frac{k_w}{[H']} = \frac{c_a - c_o}{c_o(a - c_a + c_o)} k_w \quad (xxi)$$

This method has been applied to amino-acids* and to amphoteric hydroxides.†

Conductance Method ‡—If one of the dissociation constants is appreciably lower than the other, then the solution of the pure ampholyte will be definitely acid or alkaline, and $[OH']$ may be neglected in comparison with $[H']$, or vice versa. Suppose the acidic constant is the greater, and $[OH']$ is neglected, then the equation for the equivalent conductance of the ampholyte (equation xii) becomes

$$\Lambda = \Lambda_{H'}[H'] + \Lambda_{A+}[A^+] + \Lambda_{A-}[A^-] \quad (xxii)$$

Further, by equation (v) neglecting $[OH']$:

$$[A^-] = [H'] + [A^+] \quad (xxiii)$$

$$\therefore \Lambda = \Lambda_{H'}[H'] + \Lambda_{A+}[A^+] + \Lambda_{A-}\{[H'] + [A^+]\} \\ = [H'](\Lambda_{H'} + \Lambda_{A-}) + [A^+](\Lambda_{A+} + \Lambda_{A-}) \quad (xxiv)$$

Let the ratio $(\Lambda_{H'} + \Lambda_{A-})/(\Lambda_{A+} + \Lambda_{A-})$ be written as r , then

$$\Lambda = \left([H'] + \frac{[A^+]}{r}\right)(\Lambda_{H'} + \Lambda_{A-}) \quad (xxv)$$

The ionic mobility (ion conductance) of the hydrogen ion is known, and the values of Λ_{A+} and Λ_{A-} for the ampholyte cation and anion

* Paul, *Arch. Pharm.*, 1901, 239, 48; Wood, *J. Chem. Soc.*, 1903, 83, 568; 1906, 89, 1839; Johnston (H.), *loc. cit.*

† Berl and Austerweil, *Z. Elektrochem.*, 1907, 13, 165; Wood, *J. Chem. Soc.*, 1908, 93, 411; 1910, 97, 878; Glasstone, *ibid.*, 1921, 119, 1689; Johnston (H. L.) *et al.*, *J. Amer. Chem. Soc.*, 1933, 55, 2311; 1936, 56, 2009.

‡ See also, Noyes and Wilson, *ibid.*, 1922, 44, 1630; Mehl and Schmidt (C. L. A.), *J. Gen. Physiol.*, 1935, 18, 467.

respectively, may be determined by conductance experiments on the salts of the ampholytes; excess of the acid is added to repress hydrolysis.* The apparent equivalent conductance of an ampholyte (Λ) is obtained by measuring the specific conductance κ , and $\Lambda = \kappa v$, where v is the volume in c.c. containing 1 gm. equiv. It is thus possible to calculate the value of $[H^+] + [A^+]/r$, where r is known. In order to proceed further, equation (vii) must be introduced in the form

$$[A^+] = \frac{[A]}{[OH^-]} k_b = \frac{[A][H^+] k_b}{k_w}$$

$$\frac{[A^+]}{[H^+]} = [A] \frac{k_b}{k_w} \quad \dots \quad (xxvi)$$

If k_b , the basic dissociation constant, is known, and $[A]$ as a first approximation is taken as equal to c , the total concentration of ampholyte, an approximate value of $[A^+]/[H^+]$ may be determined; since $[H^+] + [A^+]/r$ is known, rough values of $[H^+]$ and $[A^+]$ may be calculated. Using these results with equation (xxiii) and the fact that

$$c = [A] + [A^+] + [A^-] \quad \dots \quad (xi)$$

a more accurate value of $[A]$ could be obtained, and hence more accurate values of $[H^+]$ and $[A^+]$ determined; if necessary the calculations can be repeated to obtain still better values. Since $[A^-] = [H^+] + [A^+]$ (equation xxiii), the accurate value of $[A^-]$ may also be found. Finally, since

$$k_a = \frac{[H^+][A^-]}{[A]}, \quad \dots \quad (iii)$$

the acidic dissociation constant may be determined. It is thus possible to evaluate k_a for an ampholyte provided k_b is known, and the acidic function is appreciably stronger than the basic; if the basic function is the stronger, then k_b may be determined if k_a is known.

Since the ion conductances Λ_{A^+} and Λ_{A^-} are generally not determinable with any accuracy, on account of hydrolysis, it is possible to make an approximation which does not involve serious errors. According to Walker, for an amino-acid $\Lambda_{H^+} + \Lambda_{A^-}$ may be taken as equal to 370–380, and $\Lambda_{A^+} + \Lambda_{A^-}$ to 65–75 recip. ohms at 25°, since the conductances of organic cations and anions are generally between 30 and 40 recip. ohms;† it follows, therefore, that the value of r may be taken as 5, approximately.

Some of the values for the apparent dissociation constants of

* Cf. Bredig, *Z. physikal. Chem.*, 1894, 13, 214.

† Bredig, *ibid.*, p. 191.

amino-acids, obtained by the methods described, are given in Table XLI.

TABLE XLI

APPARENT DISSOCIATION CONSTANTS OF AMINO-ACIDS AT 25°.

	k_a	k_b
Alanine .	2.0×10^{-10}	$2.2 \times$
Alanylglycine .	0.66×10^{-8}	1.3×10^{-11}
Asparagine .	1.35×10^{-9}	1.5×10^{-12}
Aspartic acid (k_1)	1.5×10^{-4}	1.2×10^{-12}
(k_2)	3.4×10^{-10}	
Glutamic acid (k_1) .	6.3×10^{-5}	1.3×10^{-12}
(k_2) .	1.6×10^{-10}	
Glycine .	1.7×10^{-10}	2.3×10^{-12}
Glycylglycine	7.4×10^{-9}	1.2×10^{-11}
Phenylalanine	7.5×10^{-10}	1.3×10^{-12}
<i>o</i> -Aminobenzoic Acid	1.1×10^{-10}	2.0×10^{-12}
<i>m</i> -Aminobenzoic Acid	1.6×10^{-5}	1.2×10^{-11}
<i>p</i> -Aminobenzoic Acid	1.2×10^{-5}	2.3×10^{-12}
Arsenious Acid .	6×10^{-10}	$1. \times 10^{-14}$

Bjerrum's Theory of Ampholytes—In addition to the positive and negative ions produced by an ampholyte, a third type of ion, carrying both a positive and a negative charge, is possible. The existence of ions of this type was suggested by Bredig,* and they have become known as 'zwitter' (i.e. hermaphrodite) ions; they are also referred to as 'ampholyte', or 'dual', ions or as 'amphions'. With amino-acids the cations and anions may be regarded as $\text{NH}_3^+\text{R}\cdot\text{COOH}$ and $\text{NH}_2\text{R}\cdot\text{COO}^-$ respectively, whereas the ampholytic ion is $\text{NH}_3^+\text{R}\cdot\text{COO}^-$. Küster† considered the behaviour of methyl orange as an indicator was best explained on the assumption that in solution it existed almost entirely as ampholyte ions, but for amino-acids in general the proportion of these ions was considered to be very small. The quantity of the dual ion present in solution would be, in any case, reckoned in with the un-ionized acid (p. 267).

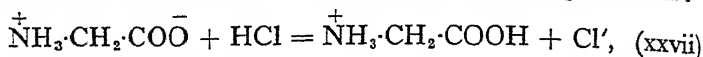
The suggestion has been made by Bjerrum‡ that nearly the whole of an amino-acid is present in solution as an ampholytic ion. The behaviour of a solution of glycine is compared with that of one of ammonium acetate; if a strong acid is added to the latter NH_4^+ ions and $\text{CH}_3\cdot\text{COOH}$ molecules result, but if alkali is added NH_3 molecules and $\text{CH}_3\cdot\text{COO}^-$ ions result. In the same way

* *Ibid.*, p. 323; *Z. Elektrochem.*, 1899, 6, 35.

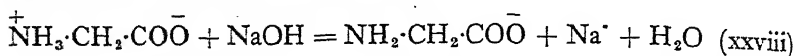
† *Z. anorg. Chem.*, 1897, 13, 135.

‡ *Z. physikal. Chem.*, 1923, 104, 147; see also Adams, *J. Amer. Chem. Soc.*, 1916, 38, 1503.

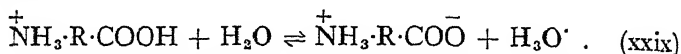
the addition of strong acid to glycine, consisting mainly of ${}^+\text{NH}_3\cdot\text{CH}_2\cdot\text{COO}^-$ ions, is said to result in the following reaction:



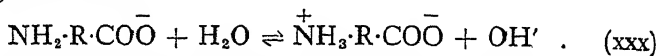
whereas the addition of alkali gives



It will be noted that these reactions are exactly the reverse of those based on the older view, according to which addition of acid affected the $-\text{NH}_2$ group, whereas alkali reacted with the $-\text{COOH}$ group. Since equation (xxvii) represents the basic function of the ampholytic ion, the acidic function of its conjugate carboxylic acid becomes evident when this equation is reversed: for the general case this may be written in the form



Similarly the basic dissociation of the amine base, conjugate to the ammonium-ion acid, is obtained by reversing equation (xxviii): it takes the general form



The actual dissociation constants k_a and k_b would then be

$$k_a = \frac{[\text{H}'] [{}^+\text{NH}_3\cdot\text{R}\cdot\text{COO}^-]}{[{}^+\text{NH}_3\cdot\text{R}\cdot\text{COOH}]} \quad \dots \quad (\text{xxxi})$$

$$\text{and} \quad k_b = \frac{[{}^+\text{NH}_3\cdot\text{R}\cdot\text{COO}^-] [\text{OH}']}{[\text{NH}_2\cdot\text{R}\cdot\text{COO}^-]} \quad (\text{xxxii})$$

Or, in general terms

$$k_a = \frac{[\text{H}'] [{}^+\text{A}^-]}{[\text{A}^+]} \quad \dots \quad (\text{xxxiii})$$

$$\text{and} \quad k_b = \frac{[{}^+\text{A}^-] [\text{OH}']}{[\text{A}^-]}, \quad (\text{xxxiv})$$

where $[{}^+\text{A}^-]$ represents the concentration of the dual ions. According to the original theory, however,

$$k_a = \frac{[\text{H}'] [\text{A}^-]}{[\text{A}]} \quad \text{and} \quad k_b = \frac{[\text{A}^+] [\text{OH}']}{[\text{A}]},$$

and since the whole of the 'un-ionized' form of the acid is assumed to exist as ampholyte ions, $[\text{A}]$ may be regarded as equal to $[{}^+\text{A}^-]$; hence

$$k_a = \frac{k_w}{k_b} \quad \text{and} \quad k_b = \frac{k_w}{k_a} \quad (\text{xxxv})$$

It is evident from equation (xxxv) and from what has been said above that the apparent acidic dissociation constant (k_a) is really the true dissociation constant of the conjugate base, ($-\text{COO}^-$), whereas the apparent basic constant (k_b) is the true value for the conjugate acid ($-\text{NH}_3^+$).

There are many advantages of Bjerrum's theory over the original view concerning amino-acids. An examination of Table XLI shows that k_a and k_b are very much smaller than would be expected from the presence of $-\text{COOH}$ and $-\text{NH}_2$ groups; k_a for glycine is about 10^{-10} , whereas the value for acetic acid is 1.8×10^{-5} . Some authors* are of the opinion that the presence of the $-\text{NH}_2$ group should actually increase the strength of the acid; this would be in keeping with Bjerrum's theory according to which k_a for glycine is actually 5×10^{-3} . The temperature coefficients of the dissociation constants, too, are much more normal than the very large values derived from the older constants.† According to Bjerrum the dual ion concept provides a theoretical interpretation of the observations of Michaelis‡ that $k_a k_b$ for an amino-acid does not exceed $\frac{1}{2} k_w$; it may also be shown that at the iso-electric point not less than 50 per cent. of an amino-acid can be un-ionized. The new theory accounts for the anomalous chemical behaviour of some amino-acids§ and also for their high melting point, sparing solubility in alcohol, and increase of solubility in water on the addition of neutral salts; the presence of the 'dual ion' accounts for these salt-like properties.

In recent years a great deal of evidence|| has accumulated to show that Bjerrum's point of view is probably correct for aliphatic amino-acids of the glycine type in aqueous solution and perhaps also for aromatic amino-sulphonic acids; aromatic amino-carboxylic acids in solution, however, contain a large proportion of simple un-ionized molecules, and amino-phenols are almost exclusively in this form. Two lines of experiment have provided results of special interest. It has been already mentioned that in changing from water to another medium, e.g. ethyl alcohol, the dissociation constants of cation acids, e.g. NH_4^+ , or of anion bases, e.g. CH_3CO_2^- , are not appreciably affected, although the values for carboxylic acids are greatly decreased and those for amines to a lesser extent.

* Vorländer, *Annalen*, 1902, 320, 99; Lowry, *Trans. Faraday Soc.*, 1923, 19, 497; see, however, Flürscheim, *ibid.*, p. 531.

† Kolthoff and Furman, *Indicators*, 1926, p. 53; Ebert, *Z. physikal. Chem.*, 1926, 121, 385; Birch and Harris, *Biochem. J.*, 1930, 24, 564.

‡ *Hydrogen Ion Concentration*, Eng. trans., 1926, p. 63.

§ Marckwald, *Ber.*, 1891, 24, 3279.

|| For summaries, see Richardson, *Proc. Roy. Soc.*, 1934, 115 B, 121; Neuberger, *ibid.*, p. 180.

The alteration in the shape of the pH-neutralization curve when the solvent is changed from water to alcohol should thus indicate which group was being affected by the addition of acid or alkali. It has been found that in alcohol the addition both of alkali and of acid to an aliphatic amino-acid gives neutralization curves corresponding to stronger acid and base respectively, although the effect is more marked with the latter: this apparent increase of strength is probably partly due to the decrease of the ionic product (see p. 228), but the results leave no doubt that the addition of acid affects the

anion base ($-\text{COO}^-$), and that alkali reacts with the cation acid ($-\text{NH}_3^+$), in accordance with equations (xxvii) and (xxviii). With the amino-benzoic acids in alcohol the addition of alkali gives a neutralization curve corresponding to an acid much weaker than in water, whereas acid addition indicates the base to be slightly weaker. This result supports the view that in aromatic amino-carboxylic acids the acidic and basic functions are exercised by the $-\text{NH}_3^+$ and $-\text{COOH}$ group, respectively, and that the concentration of dual ions is much less than in aliphatic amino-acids.*

The addition of formaldehyde to an aqueous solution of an amine is known to decrease its basic properties: the dissociation constant of the $-\text{NH}_3^+$ base is thus decreased whereas that of the conjugate acid $-\text{NH}_3^+$ should be increased. It has been found† that the presence of formaldehyde produces no change in the pH-neutralization curve of an aliphatic amino-acid on the addition of acid, but when alkali is added the curve is moved in the direction of increased strength of the acid being neutralized. With *p*-amino-benzoic acid and *p*-amino-phenol the titration curve with alkali is unaffected, but that with acid suggests that a weaker base is present. These observations strongly support the 'zwitterion' theory of Bjerrum for aliphatic amino-acids. Other evidence for this point of view has been obtained from measurements of dielectric constant of aqueous solutions,‡ from the effect on the pH of buffer solutions,§ from the variation of activity coefficient with the ionic strength ||

* Jukes and Schmidt (C. L. A.), *J. Biol. Chem.*, 1934, **105**, 359; Neuberger, *loc. cit.*; Ogston and Brown, *loc. cit.*

† Harris, *Biochem. J.*, 1930, **24**, 1080, 1086.

‡ Blüh, *Z. physikal. Chem.*, 1923, **106**, 341; Blüh and Kroczeck, *ibid.*, 1934, **B 27**, 263, 270; 1935, **B 28**, 410; Devoto, *Gazzetta*, 1931, **61**, 897; 1933, **63**, 247; *Z. Elektrochem.*, 1934, **40**, 490; Frankenthal, *Z. physikal. Chem.*, 1932, **B 19**, 328; Wyman and McMeekin, *J. Amer. Chem. Soc.*, 1933, **55**, 908, 915; Wyman, *ibid.*, 1934, **56**, 536; see also Kuhn and Martin (H.), *Ber.*, 1934, **67**, 1526.

§ Borsook and MacFadyen, *J. Gen. Physiol.*, 1930, **13**, 509.

|| Scatchard and Kirkwood, *Physikal. Z.*, 1932, **33**, 297.

—it should be a direct function of the latter instead of its square-root as for ordinary ions—and from a comparison of the dissociation constant of the amino-acid and that of its ethyl ester.*

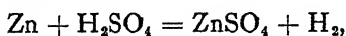
It may be pointed out in conclusion that even if the new theory of the constitution of amino-acid ampholytes is applicable in many cases, the results for k_a and k_b determined on the basis of the old theory will still be significant although their interpretation will be different; in the same way the values for concentrations of the simple ions calculated by means of these constants will still be correct.

* Ebert, *loc. cit.*; Edsall and Blanchard, *J. Amer. Chem. Soc.*, 1933, 55, 2337.

CHAPTER XII

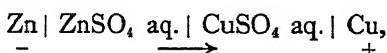
REVERSIBLE CELLS—I

A GALVANIC or voltaic cell, or element, is a system by means of which chemical energy is converted into electrical energy; such cells generally consist of one or more liquid conductors, e.g. electrolytic solutions, into which dip two electrodes of metal. Although two electrodes are essential in a cell in order that there may be a flow of electric current, they need not necessarily be of different metals. One of the simplest voltaic cells consists of zinc and copper electrodes dipping in dilute sulphuric acid; the zinc dissolves and hydrogen is deposited on the copper when the cell produces current. The chemical reaction occurring in this system is

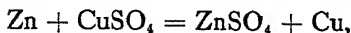


or alternatively $\text{Zn} + 2\text{H}^+ = \text{Zn}^{++} + \text{H}_2.$

A voltaic cell of a different type is obtained by dipping a piece of zinc in zinc sulphate solution and a strip of copper in copper sulphate solution; the two solutions are generally separated by placing one inside a porous pot and the other in a surrounding vessel. Such a system is known as the Daniell cell, and when the zinc and copper electrodes are connected current flows from the latter to the former through the external circuit. The cell may be represented as



the direction of the current *through* the cell being shown by the arrow.* During the passage of current the zinc (negative) electrode dissolves but copper is deposited on the positive copper electrode; the chemical reaction occurring in the cell may be written



or better, $\text{Zn} + \text{Cu}^{++} = \text{Zn}^{++} + \text{Cu}.$

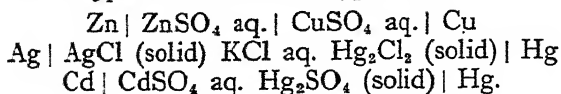
If the simple voltaic cell and the Daniell cell are compared, one important difference, among others, may be noted. On pass-

* The convention of representing the flow of electricity *through* the cell is frequently used, and will be adopted in this book.

ing current from an external source through the former, the copper electrode will dissolve and hydrogen will be liberated at the zinc electrode ; this is not the reverse of the reaction occurring when the cell is producing current, and hence this voltaic element cannot be regarded in any sense as reversible. The Daniell cell, on the other hand, belongs to the class of **reversible cells** ; if this element is connected to an outside source of *E.M.F.* exactly equal to that of the cell itself no chemical reaction will occur within it. If the external *E.M.F.* is decreased by an infinitesimally small amount current will flow from the Daniell cell, and the normal cell reaction will occur ; but if the external *E.M.F.* is increased very slightly the current passes through the Daniell cell in the reverse direction and the reverse chemical reaction occurs, i.e. copper dissolves and zinc is deposited. The conditions satisfied by the Daniell cell are those required from any *reversible* galvanic element ; it is essential to note that such cells are only reversible when infinitesimally small currents are passing through the system, which thus remains in a condition of equilibrium. A reversible cell working in this way is producing 'maximum work' and so may be studied thermodynamically.

Types of Reversible Electrodes—In general, reversible electrodes are of three types ; the first type consists of a metal dipping into a solution containing its ions, e.g. silver in a solution of silver nitrate. Such an electrode is reversible with respect to the ions of the metal ; hydrogen may be used to form an electrode of this type. The second group involves electrodes made by dipping an unattackable metal, e.g. platinum, in a solution containing ions in two valency states, e.g. ferrous and ferric ; the reversible change occurring at such electrodes involves oxidation and reduction. The third type of electrode is reversible with respect to anions ; oxygen and chlorine electrodes belong to this group, but they are not of great importance in comparison with those consisting of a metal, in contact with one of its insoluble salts, immersed in a solution of soluble salt of the same anion, e.g. mercury—solid mercurous chloride—potassium chloride solution. If current is passed from electrode to electrolyte mercury dissolves to form mercurous ions ; these unite with chlorine ions from the solution and form insoluble mercurous chloride. The net result is the removal of chlorine ions from solution. On passing current in the opposite direction mercurous ions are deposited ; the solution becomes unsaturated, some mercurous chloride dissolves, but there remains an equivalent amount of chlorine ions in excess. The system thus behaves as a reversible chlorine electrode ; reversible bromine, iodine and oxygen electrodes may be obtained in a similar manner. A reversible cell is always made up of two

reversible electrodes, or half-elements; these half-elements may be of the same type or of different types, e.g.



Other cells consisting of two electrodes of the same metal dipping into solutions of different concentrations are also reversible; the electrical energy produced in these cells is balanced by osmotic work (p. 289).

Energy Changes—Energy is always expressed in terms of the product of a capacity and an intensity factor; for electrical energy the intensity factor is the *E.M.F.* and the capacity factor is the quantity of electricity passing. If the former is expressed

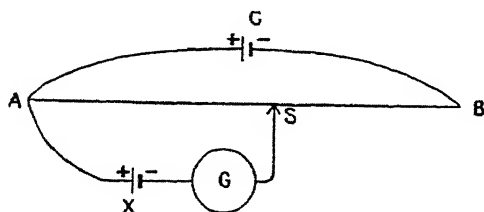


FIG. 19.—The Poggendorff compensation method

in volts and the latter in coulombs the electrical energy is in volt-coulombs, or joules; 1 joule is equivalent to 10^7 ergs or 0.2390 calories (p. 5). In order to determine the amount of energy produced by a galvanic cell it is necessary to know the quantity of electricity passing and the *E.M.F.*; the former may be determined from the chemical reaction occurring in the cell, since 1 faraday (96,500 coulombs) is involved in the dissolution or deposition of 1 gm. equiv. of any ion. The method of measuring the *E.M.F.* of a galvanic cell will now be described.

Measurement of *E.M.F.*—The principle generally used is that of the Poggendorff compensation method. A 'working cell' C, Fig. 19, usually an accumulator of constant *E.M.F.*, is connected across the ends of a uniform wire AB, of high resistance. The cell X under examination is connected to A, with the poles in the same direction as the cell C, and then through a galvanometer G to a sliding contact S, which can be moved along AB. The position of S is so adjusted that no current flows through the galvanometer; then the fall of potential along AS due to the cell C is exactly balanced by the *E.M.F.* (E_x) of X. In order to determine the potential fall along AB the cell X is replaced by a standard cell, e.g. a Weston element, of accurately known *E.M.F.* (E_w), and

the slider adjusted until a point of balance is reached at S' ; the fall of potential along AS' is then equal to E_w , and since the wire AB is uniform

$$E_x = \frac{AS}{AS'} \times E_w.$$

By means of this equation the value of E_x may be calculated.

The *E.M.F.* of the working cell C must be greater than that of the cell being examined; a two-volt accumulator is satisfactory for most purposes. If much current is drawn from this cell its *E.M.F.* is liable to decrease; hence the fall of potential along AB should be checked at frequent intervals. The wire AB , generally called the 'potentiometer wire', may be of platinum, or platinum-iridium, stretched tightly along a graduated metre scale; the sliding contact maker may have a platinum knife-edge and the point of contact can be read off with an accuracy of at least 0.5 mm., representing an error of 1 millivolt if C is 2 volts. For accurate work the wire may be replaced by two resistance boxes; the contact S is fixed at the point where the two boxes are joined, and the cell C is connected across both boxes. The resistances in the boxes are varied in ratio, but the *sum is kept constant*. If R_x is the resistance taken from the left-hand box, across which the cell X is connected, when a balance is obtained, and R_w the resistance taken out when the standard Weston cell is used, then

$$E_x = \frac{R_x}{R_w} \times E_w.$$

As a rule the sum of the resistances used is about 11,000 ohms, and with a working cell of 2 volts, each ohm represents 0.2 millivolt. A number of special potentiometers are on the market which allow *E.M.F.*'s to be read off directly with an accuracy of 0.1 millivolt; the Poggendorff compensation principle is invariably employed. As the null-point detector a mirror galvanometer with a high megohm sensitivity is used when great accuracy is desired. For less precise work the capillary electrometer may be employed; it has many advantages, e.g. insensitivity to electrical and magnetic disturbances, high resistance and consequent small drain on the current from the experimental cell, but it is generally only sensitive to a millivolt and is liable to behave erratically in damp weather. In recent years there has been a tendency to replace the capillary electrometer by cheap pointer galvanometers.*

At one time the Clark cell, consisting of a zinc (or 10 per cent. zinc amalgam) electrode in a saturated solution of $ZnSO_4 \cdot 7H_2O$ and a mercury electrode covered with mercurous sulphate paste

* For modifications necessary with cells of high resistance, see p. 382.

in the same solution, was the chief standard used in potentiometric work.* The *E.M.F.* at a temperature of $t^{\circ}\text{C.}$ is given by the expression :

$$E_t = 1.4328 - 0.00119(t - 15) - 0.000007(t - 15)^2.$$

Owing to the high temperature coefficient of this cell—about 0.0012 volt per degree—it has been replaced almost completely by the Weston cell. This element has one electrode of 12.5 per cent. cadmium amalgam covered with crystals of $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ in a saturated solution of the salt ; the other electrode is of mercury and is covered with solid mercurous sulphate. The *E.M.F.* in 'International volts' of the Weston cell at any temperature may be calculated from the formula : †

$$E_t = 1.018300 - 0.0000406(t - 20) - 0.00000095(t - 20)^2 \\ + 0.00000001(t - 20)^3 ;$$

the temperature coefficient is small enough to be neglected for most purposes. The change of *E.M.F.* with age is extremely small ; ‡ hence the element forms a valuable standard. A form of the Weston cell containing an unsaturated solution of cadmium sulphate has been recommended as a secondary standard : its temperature coefficient is even smaller than that of the saturated cell,§ but the *E.M.F.* is more liable to change in the course of time.||

In the measurement of *E.M.F.*'s by the Poggendorff method, it is apparent that the experimental cell is producing no current at the point of balance, and so the *E.M.F.* may be regarded as the reversible value. If appreciable currents are drawn from the cell during measurement it may be disturbed from its equilibrium condition, and the determined value will not represent the reversible *E.M.F.* of the element.**

Relation of Chemical and Electrical Energy—It was originally suggested by Helmholtz and by Thomson (Lord Kelvin)

* Jaeger, *Ann. Physik*, 1897, **63**, 354.

† Wolf and Waters, *Bull. Bureau Stand.*, 1908, **5**, 309 ; see also Vigoureux and Watts, *Proc. Physical Soc.*, 1933, **45**, 172. For further references, see *International Critical Tables*, 1929, Vol. VI, p. 312 ; Ostwald-Drucker, *Handbuch der allgemeinen Chemie*, Vol. VIII, Part I, 1930, p. 184 (Kremann and R. Müller).

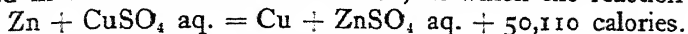
‡ See, however, Cohen and Moesveld, *Z. physikal. Chem.*, 1920, **95**, 280 ; 1923, **104**, 403 ; and reply by Jaeger and von Steinwehr, *ibid.*, 1921, **97**, 319.

§ Cf. Vosburgh and Eppley, *J. Amer. Chem. Soc.*, 1923, **45**, 2268.

|| Vinal, *Trans. Amer. Electrochem. Soc.*, 1928, **54**, 247. For other recent work with saturated and unsaturated cells, see Vosburgh and Elmore, *J. Amer. Chem. Soc.*, 1931, **53**, 2819 ; Vinal *et al.*, *Bur. Standards J. Res.*, 1933, **11**, 255 ; *Trans. Amer. Electrochem. Soc.*, 1935, **68**, 203.

** The use of a thermionic-valve potentiometer (p. 382), prevents the flow of appreciable currents.

that in a galvanic cell the heat evolved in the chemical reaction occurring during the passage of current was a direct measure of the *E.M.F.* This view involved the assumption that the chemical energy was converted completely into electrical energy; it was tested in the case of the Daniell cell, in which the reaction is



The process involves the dissolution of 1 gm. atom, i.e. 2 gm. equiv. of zinc, and the deposition of 2 gm. equiv. of copper; hence 2 faradays, i.e. $2 \times 96,500$ coulombs, of electricity pass through the cell. If E (volts) is the *E.M.F.* then the electrical work performed by the cell is $2 \times 96,500 \times E$ volt-coulombs (joules). The chemical energy transformed in the Daniell cell is 50,110 calories, or $50,110 \times 4.184$ joules; if the principle of complete equality of chemical and electrical energy applies, then

$$2 \times 96,500 \times E = 50,110 \times 4.184 \\ \therefore E = 1.09 \text{ volts.}$$

The actual value of the *E.M.F.* of the Daniell cell depends on the concentrations of the solutions, but it is approximately 1.10 volts. This, and other, cases appeared to support the Thomson principle, but investigations by Braun, and the thermodynamic studies of Gibbs and Helmholtz* showed it to be insufficient, and to apply only if the galvanic cell neither gave out heat nor absorbed heat from its surroundings whilst producing current. The correct relationship between the heat involved in the chemical reaction and the electrical energy produced in a *reversible* cell is given by the Gibbs-Helmholtz equation in the form:

$$E = -\frac{4.184\Delta H}{nF} + T\frac{dE}{dT} \quad (i)$$

Where E is the *E.M.F.* of the cell, dE/dT its temperature coefficient, nF the number of coulombs passing through the cell, and ΔH calories represents the heat *absorbed* in the corresponding chemical reaction at constant pressure. This equation indicates that if the temperature coefficient of the *E.M.F.* of the cell is positive, the electrical energy produced is greater than the chemical energy expended, and a quantity of heat equivalent to $nFT\frac{dE}{dT}$ is absorbed from the surroundings; on the other hand, when dE/dT is negative, an amount of heat equivalent to $nFT\frac{dE}{dT}$ is radiated to the surroundings, if the temperature of the cell remains constant. If the temperature coefficient is zero the electrical and chemical

* Braun, *Ann. Physik*, 1882, 17, 593; Gibbs, *Trans. Connecticut Acad.*, 1875, 3, 108, 248; Helmholtz, *Sitzungsber. Berl. Akad.*, 1882, 22.

energies are identical, and it is only in this limited case that the Thomson principle holds; in the Daniell cell dE/dT is very small, and the *E.M.F.* calculated as equivalent to the chemical energy is almost identical with the true value. The accuracy of the Gibbs-Helmholtz equation as applied to reversible cells was verified qualitatively by Czapski* and by Gockel,† and quantitatively by Jahn,‡ and others§; some of the results obtained are quoted in Table XLII.

TABLE XLII

EXPERIMENTAL CONFIRMATION OF THE GIBBS-HELMHOLTZ EQUATION

Cell and Reaction.	<i>E.M.F.</i>	dE/dT .	ΔH Calories.	
			Calculated.	Observed.
$\text{Cu} \mid \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \text{ aq.} \parallel$ $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \text{ aq.} \mid \text{Pb.}$ $\text{Pb} + \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ $= \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{Cu}$	0.470 at 0°	3.85×10^{-4}	-16,900	-17,532
$\text{Ag} \mid \text{AgCl}$ $\text{ZnCl}_2 + 100 \text{ H}_2\text{O} \mid \text{Zn.}$ $\text{Zn} + 2\text{AgCl}$ $= \text{ZnCl}_2 + 2\text{Ag}$	1.015 at 0°	-4.02×10^{-4}	-51,989	-52,046
$\text{Hg} \mid \text{Hg}_2\text{Cl}_2, 0.01 \text{ N-KCl} \parallel$ $0.01 \text{ N-KOH Hg}_2\text{O} \mid \text{Hg.}$ $\text{Hg}_2\text{Cl}_2 + 2\text{KOH}$ $= 2\text{KCl} + \text{H}_2\text{O} + \text{Hg}_2\text{O}$	0.1483 at 18.5°	8.37×10^{-4}	3,710	3,280
$\text{Cu} \mid \text{CuSO}_4 \text{ aq. satd.} \parallel$ $\text{ZnSO}_4 \text{ aq. satd.} \mid \text{Zn.}$ $\text{Zn} + \text{CuSO}_4 = \text{ZnSO}_4 + \text{Cu}$	1.0934 at 15°	4.29×10^{-4}	-56,089	-55,189

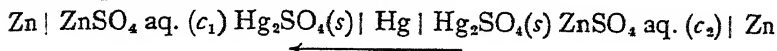
The agreement between observed and calculated values confirms the applicability of the Gibbs-Helmholtz equation, and suggests a method for calculating the heat of a reaction from measurements of *E.M.F.* and of its temperature coefficient. This method has been frequently used, and in many instances the results have been claimed to be more accurate than those obtained by thermochemical measurements; || special precautions must, however, be taken to

* *Ann. Physik*, 1884, 21, 203.† *Ibid.*, 1885, 24, 618.‡ *Ibid.*, 1886, 28, 21; 1893, 50, 189.§ e.g. Bugarsky, *Z. anorg. Chem.*, 1897, 14, 145; Cohen, Chattaway and Tombrock, *Z. physikal. Chem.*, 1907, 60, 706.|| See, for example, Taylor (H. S.) and Perrot, *J. Amer. Chem. Soc.*, 1921, 43, 48.

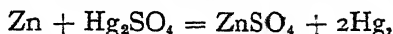
REVERSIBLE CELLS—I

obtain a very accurate value for dE/dT , and also to eliminate 'liquid junction potentials' * (p. 316). If it is desired to calculate the *E.M.F.* of a cell from a knowledge of the heat of reaction use must be made of the Nernst Heat Theorem; † in some instances it is possible to calculate from thermal data the potentials of electrodes which are difficult to measure directly. ‡

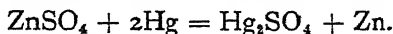
Concentration Cells without Transport—The *E.M.F.* of a Clark cell, $\overset{+}{\text{Hg}} | \text{Hg}_2\text{SO}_4(s) | \text{ZnSO}_4 \text{ aq.} | \text{Zn}$, depends on the concentration of the zinc sulphate solution; § for a definite concentration c_1 the *E.M.F.* has a definite value E_1 , whereas if the solution is *diluted* to a concentration c_2 it is found that the *E.M.F.* of the cell is *increased* to E_2 . If two Clark cells containing zinc sulphate solutions of concentration c_1 and c_2 respectively, are connected up in opposition to one another, thus:



the resulting system has a net *E.M.F.* of $E_2 - E_1$; the electrode dipping in the more concentrated zinc sulphate solution (c_1) is found to be the positive electrode of the composite cell. In the right-hand half of the element, zinc dissolves, leaving the electrode negatively charged, and the chemical reaction occurring is



whereas in the left-hand cell the conditions are reversed and the reaction is



The net result of drawing current from the whole system is that zinc and solid mercurous sulphate are removed, and equivalent amounts of zinc sulphate and mercury are formed, in one half-cell; the reverse process occurs in the other cell, and there is no resultant chemical transformation. The only permanent change in the system is the removal of zinc sulphate from the concentrated solution and its formation in the dilute solution. The electrical energy of the complete cell cannot be due to the transformation of chemical energy; it must be equivalent to the change of free energy—since the cell is reversible—resulting from the osmotic transfer

* See Webb, *J. Physical Chem.*, 1925, 29, 816.

† Halla, *Z. Elektrochem.*, 1908, 14, 411; 1911, 17, 179; Allmand, *J. Chem. Soc.*, 1909, 95, 2151; Pollitzer, *Z. Elektrochem.*, 1911, 17, 5; 1913, 19, 515; *Z. physikal. Chem.*, 1911, 78, 374; Braune and Koref, *Z. anorg. Chem.*, 1914, 87, 175; Taylor, *J. Amer. Chem. Soc.*, 1916, 38, 2295.

‡ See Tamele, *J. Physical Chem.*, 1924, 28, 502; Drossbach, *Z. Elektrochem.*, 1927, 33, 114.

§ If the solution is saturated and solid salt is present the symbol (s) will be used.

of zinc sulphate from the more concentrated to the more dilute solution. The actual energy is drawn from the surroundings, or from the system itself if it is isolated; in the latter case the temperature will fall. The arrangement described here is known as a **concentration cell without transport**; the *E.M.F.* depends on the concentrations of the two solutions, but as they are not in direct contact zinc sulphate is not transported directly from one solution to the other.

Since the concentration cell under discussion works perfectly reversibly, thermodynamic principles may be used to calculate its *E.M.F.* Suppose two faradays of electricity pass through the whole cell, then two gm. equivs. (one gm. atom) of zinc will dissolve at the right-hand electrode and be deposited at the other; the concentration of the dilute solution will thus be increased by 1 gm. mol. of zinc sulphate, and that of the more concentrated solution will be diminished by the same amount. The production of two faradays is thus accompanied by the transfer of 1 gm. ion of zinc ions and 1 gm. ion of sulphate ions from the solution of concentration c_1 to that of concentration c_2 . The free energy change for the transfer of the positive ions, may be written

$$-\Delta G_+ = RT \ln \frac{(a_+)_1}{(a_+)_2}$$

where $(a_+)_1$ and $(a_+)_2$ are the activities of the zinc ions in the concentrated and dilute solutions, respectively. Similarly the change in free energy accompanying the transfer of 1 gm. ion of the negative ions is correspondingly

$$-\Delta G_- = RT \ln \frac{(a_-)_1}{(a_-)_2} \quad (\text{iii})$$

where $(a_-)_1$ and $(a_-)_2$ represent the activities of the sulphate ions in the two solutions. The total free energy change (ΔG) is then the sum of ΔG_+ and ΔG_- : that is

$$-\Delta G = 2RT \ln \frac{a_1}{a_2} \quad \dots \quad (\text{iv})$$

where a_1 and a_2 are the *mean* activities of zinc sulphate in the solutions of concentration c_1 and c_2 , respectively. The electrical work corresponding to the passage of two faradays is $2EF$ volt-coulombs, where E is the *E.M.F.* of the complete cell; hence

$$-\Delta G = 2EF, \quad \dots \quad (\text{v})$$

and from equations (iv) and (v) it follows that

$$E = \frac{RT}{F} \ln \frac{a_1}{a_2} \quad \dots \quad (\text{vi})$$

Replacing the activity (a) by the product of the concentration (c)

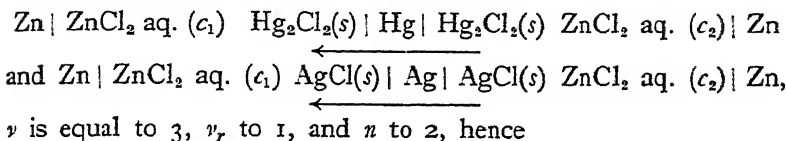
and the stoichiometric activity coefficient (γ), equation (vi) takes the form

$$E = \frac{RT}{F} \ln \frac{\gamma_1 c_1}{\gamma_2 c_2} \quad (\text{vii})$$

γ_1 and γ_2 being the activity coefficients in the two solutions. For approximate purposes the activity coefficients are sometimes replaced by the conductance ratios. The general equation for the *E.M.F.* of any concentration cell without transport is

$$E = \frac{\nu}{n} \frac{RT}{F} \ln \frac{\gamma_1 c_1}{\gamma_2 c_2} \quad (\text{viii})$$

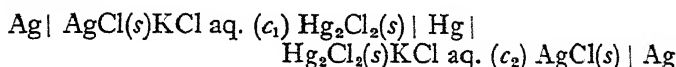
where n is the valency of the ion with respect to which the extreme electrodes are reversible, ν , the number of these ions, and ν the total number of ions produced by the ionization of each molecule of salt transferred. Thus, for the cells



ν is equal to 3, ν_r to 1, and n to 2, hence

$$E = \frac{3RT}{2F} \ln \frac{\gamma_1 c_1}{\gamma_2 c_2} \quad \dots \dots \dots (\text{ix})$$

For the cell

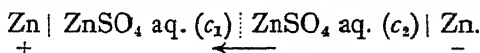


the salt transferred is potassium chloride, hence $\nu = 2$; but the electrodes are reversible with respect to the chlorine ion and $n = 1$, therefore

$$E = \frac{2RT}{F} \ln \frac{\gamma_2 c_2}{\gamma_1 c_1} \quad (\text{x})$$

The quantity ν_r here refers to the chlorine ions and is equal to unity. The direction of the *E.M.F.* is opposite to that in the other cells, and so the fraction $\gamma_2 c_2 / \gamma_1 c_1$ is inverted.

Concentration Cells with Transport—If the intermediate electrode, i.e., $\text{Hg}_2\text{SO}_4(s) | \text{Hg} | \text{Hg}_2\text{SO}_4(s)$, is removed from the double Clark cell (p. 289), there remains the element:



In this cell the two solutions are in contact, and there is a *direct* transport of zinc sulphate from the more concentrated (c_1) to the more dilute solution (c_2); as before the zinc electrode in the concentrated solution is the positive and has zinc deposited on it,

whereas the other electrode dissolves. The cell is still reversible, and the electrical energy is equivalent to the free energy change accompanying the osmotic transfer of an appropriate amount of zinc sulphate from the more concentrated to the more dilute solution. When electricity passes through this cell the fraction of the total current carried by anions and cations respectively, is equal to their transport numbers, n_a and n_c ; hence for the passage of one faraday n_c gm. equiv. of cations (zinc) migrate out of the cathode into the anode compartment, i.e. right to left, whilst at the same time 1 gm. equiv. of zinc dissolves off from the negative electrode. The concentration of the more dilute solution is thus increased by $1 - n_c (= n_a)$ gm. equiv. of zinc ions; the more concentrated solution is at the same time impoverished by this amount since n_c gm. equiv. migrate in and 1 gm. equiv. of zinc is deposited on the left-hand (positive) electrode. At the same time n_a gm. equiv. of anions (SO_4^{--}) are transferred from anode to cathode solutions, i.e. from left to right, in a direction opposite to that of the flow of current through the cell. The net result of the passage of one faraday of electricity is that the concentration of the dilute solution (c_2) is increased by n_a gm. equiv. of zinc sulphate, and the concentrated solution (c_1) is depleted by this amount. Hence when two faradays pass through the cell n_a gm. mols. of zinc sulphate, in the form of ions, are transferred from the solution c_1 to the solution c_2 . By the same method as that used in connection with the concentration cell without transport, it is readily shown (cf. equation iv) that the free energy change is

$$\begin{aligned} -\Delta G &= 2n_a RT \ln \frac{a_1}{a_2} * \\ &= 2n_a RT \ln \frac{\gamma_1 c_1}{\gamma_2 c_2}. \end{aligned}$$

Since the electrical work accompanying the passage of two faradays is $2EF$, it follows that

$$E = n_a \frac{RT}{F} \ln \frac{\gamma_1 c_1}{\gamma_2 c_2} \quad (\text{xi})$$

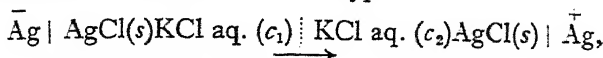
In general for any concentration cell with transport, reversible with respect to *cations* of valency n ,

$$E = n_a \frac{\nu}{\nu_+} \frac{RT}{nF} \ln \frac{\gamma_1 c_1}{\gamma_2 c_2} \quad \dots \dots \dots (\text{xii})$$

where ν is the total number of ions and ν_+ the number of positive

* Strictly speaking this assumes that the transport number n_a remains constant over the range of concentration c_1 to c_2 (cf. p. 371).

ions produced by 1 molecule of the solute of variable concentration on dissociation. For a cell of the type



which is reversible with respect to the chlorine ion, it may be shown that for the passage of 1 faraday of electricity n_e gm. mols. of potassium chloride are transferred from more concentrated (c_1) to more dilute solution (c_2); hence

$$E = n_c \frac{\nu}{\nu_-} \cdot \frac{RT}{nF} \ln \frac{\gamma_2 c_2}{\gamma_1 c_1} \quad (\text{xiii})$$

where ν_- is the number of negative ions resulting from the ionization of 1 molecule of electrolyte. The fraction $\gamma_2 c_2 / \gamma_1 c_1$ has again been reversed to show that the flow of current is in the reverse direction from that of the previous cell.

Nernst's Theory of Solution Pressure—An electrical potential difference in a conducting system only appears at the surface of separation of two phases; hence in the zinc sulphate concentration cell discussed the three interfaces at which potential differences may occur are:

- (i) $\text{Zn} \mid \text{ZnSO}_4 \text{ aq. } (c_1)$,
- (ii) $\text{ZnSO}_4 \text{ aq. } (c_1) \parallel \text{ZnSO}_4 \text{ aq. } (c_2)$,
- and (iii) $\text{ZnSO}_4 \text{ aq. } (c_2) \mid \text{Zn}$.

A mechanism for the production of a potential difference at the surface of separation between a metal and a solution containing its ions was first suggested by Nernst; * according to this view all metals possess a property called **solution pressure**, or 'solution tension', in virtue of which they tend to pass into solution as positive ions. If, for example, a piece of zinc is dipped into pure water a number of positive ions pass into the water under the stress of the solution pressure of the metal; the latter is thus left with a negative charge, and a difference of potential exists between the metal and liquid. Since the ions carry a comparatively large charge they do not move away from the oppositely charged metal but form an electrical 'double layer'. The attraction of the opposite charges prevents the further expulsion of positive ions from the metal and an equilibrium, with a definite potential difference, is rapidly established when only very few ions of the metal have entered the liquid. For this reason, although the solution pressure may be considerable, the amount of metal dissolved is so small as not to be detectable by analytical methods. In developing the theory Nernst assumed that the tendency for the metal to ionize was opposed by the reverse tendency of the ions in solution, as a consequence of their

* *Z. physikal. Chem.*, 1889, 4, 129.

osmotic pressure, to leave the solution and be deposited on the solid metal. The predominating tendency, and the potential difference between the metal and solution of its ions, depend on the relative magnitudes of solution pressure and osmotic pressure. In this connection three cases are possible.

Case I.—The solution pressure (P) of the metal is greater than the osmotic pressure of the ions of the metal (P) in

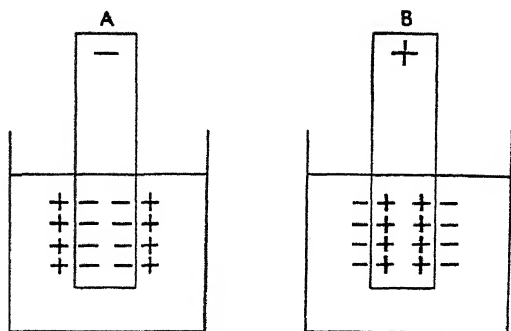


FIG. 20.—Illustration of Nernst's solution pressure theory

solution—In this case the tendency for the ions to leave the metal will be greater than the reverse; the net result will be that positive ions will enter the liquid and leave the metal negatively charged. A difference of potential results in which the metal is negative with respect to the solution (Fig. 20, A). The metals giving the most basic oxides, i.e. the so-called most electropositive metals, have high solution pressures; these are generally negatively charged in solutions of their salts, e.g. manganese, zinc, cadmium and the alkali metals.

Case II.—The solution pressure of the metal is less than the osmotic pressure of the ions of the metal in solution—The tendency for the ions to leave the solution now predominates over the reverse effect; the metal thus acquires a positive charge and the solution is left negatively charged (Fig. 20, B). Metals of low solution pressure, e.g. copper, silver, mercury, gold, will thus be generally positively charged with respect to solutions of their ions. In some cases, however, the ionic concentration may be reduced to such an extent that the osmotic pressure is less than the solution pressure of the metal; the sign of the electrode potential is then reversed.

Case III.—The solution pressure of the metal is equal to the osmotic pressure of the ions of the metal in solution—The tendency for ions to leave the metal is exactly balanced by their desire to leave the solution; no double layer is formed and

no difference of potential exists between metal and solution. Such a system is sometimes called a 'null electrode'.

Although solution pressure has been discussed from the standpoint of metals, i.e. substances yielding positive ions, it is also applicable to materials capable of producing negative ions. It will be shown later that oxygen and chlorine electrodes may be obtained with a definite tendency to send OH' and Cl' ions, respectively, into solution. If the solution pressure exceeds the osmotic pressure of the ions the electrode becomes *positively* charged; but if the osmotic pressure is the greater the electrode attains a negative potential with respect to the solution.

The solution pressure of a given electrode material depends on its physical condition; fine crystals of a metal have a higher solution pressure than do large crystals, and so the former will have a more negative potential in the same solution. This fact is of importance in connection with problems of corrosion (p. 504). Two allotropic forms of a metal have different solution pressures; the metastable form has the higher value and so acquires a more negative potential (cf. p. 373). The solution pressure in an amalgam of a metal more base than mercury is less than that of the pure metal; the more dilute the amalgam the less the solution pressure. In the same way the solution pressure of a gas, e.g. hydrogen, oxygen, depends on the pressure of the gas (p. 310). The solution pressure of an element varies with the nature of the solvent medium containing the ions (p. 361).

Potential Difference at a Reversible Electrode—It has already been seen qualitatively that the potential of an electrode* depends on the concentration of its own ions in solution; the quantitative expression for the potential of a reversible electrode (metal|ions), may be obtained as follows. Consider a metal of valency n dipping into a solution in which P is the osmotic pressure of its ions; let P be the solution pressure of the metal, and π the actual difference of potential between metal and solution. By connecting this electrode with another, more positive, electrode which need not be considered further, the resulting cell may be made to produce n faradays of electricity and 1 gm. ion of metal will dissolve as a consequence; the expenditure of electrical energy at the electrode under consideration will be πnF volt-coulombs. Suppose now the solution is diluted so that the osmotic pressure is reduced to $P - dP$, the difference of potential between metal and solution is now changed to $\pi - d\pi$; hence in order to cause the dissolution of 1 gm. ion of metal the electrical energy to be

* Strictly speaking the term 'potential difference between the electrode and electrolyte' should be used; this is almost invariably abbreviated to 'electrode potential' or 'potential of electrode'.

expended is $(\pi - d\pi)nF$ volt-coulombs. This difference in electrical energy ($nFd\pi$) must be equal to the free energy changes resulting from the transfer of 1 gm. ion of the metal from the solution of osmotic pressure P to that of osmotic pressure $P - dP$; that is

$$nFd\pi = RT \ln \frac{P}{P - dP} \quad \dots \quad (xiv)$$

$$: RT \frac{dP}{P} \quad (xv)$$

provided the solutions are ideal and the osmotic pressures are directly proportional to the activities of the ions. On integrating equation (xv) it follows that

$$nF\pi = RT \ln P + K, \quad \dots \quad (xvi)$$

where K is the integration constant. When the osmotic pressure (P) of the solution is equal to the solution pressure (\bar{P}) of the metal, there is no difference of potential between metal and solution; hence $\pi = 0$, and

$$0 = RT \ln \bar{P} + K \\ \therefore K = -RT \ln \bar{P} \quad \dots \quad (xvii)$$

In general, therefore, $nF\pi = RT \ln \frac{P}{\bar{P}}$

$$\therefore \pi = \frac{RT}{nF} \ln \frac{P}{\bar{P}} \quad (xviii)$$

This expression is known as the Nernst equation for the potential of an electrode

Sign of Electrode Potential—The Nernst equation does not actually include the sign of the potential and in this connection a definite convention is necessary. The system generally adopted in Europe, and by many writers in the U.S.A., is to state the potential difference of the *metal* with respect to the solution; in other words the sign, in general, is that which the metal assumes according to the theory of solution pressure. Thus metals with low solution pressures are generally positive, and metals with high solution pressures have negative potentials by the convention; the more concentrated the solution in ions of the metal the more positive will be the potential. The formula as written above (equation xviii) complies with these requirements for an electrode yielding *positive ions*, and hence includes the sign of the potential in agreement with the convention adopted in this book.*

* It is important to note that in the older German and in more recent American literature the opposite convention is adopted.

Equations for Electrode Potential—Equation (xviii) may be written in a number of ways, thus

$$\pi = \frac{RT}{nF} \ln P - \frac{RT}{nF} \ln P.$$

At constant temperature the expression $RT/nF \ln P$ is constant for a given metal; hence

$$\pi = \frac{RT}{nF} \ln P + \text{constant} \quad \dots \quad (\text{xix})$$

Further, the gas laws may be written in the form $P = RTc$, where c is the concentration of the positive ions in the solution complying with the requirements of the laws; actually the equation should be $P = RTa_+$, where a_+ is the activity of the reversible ions. At constant temperature, therefore, $P = ka_+$, and

$$\pi = \frac{RT}{nF} \ln a_+ + \text{constant} (\pi_0) \quad \dots \quad (\text{xx})$$

The significance of the constant π_0 will be discussed later. In the form of the equation used before the introduction of the activity concept, the concentration of the ions (c) was used instead of the activity (a). The equation may be simplified by using logarithms to the base of ten and inserting the known values of the constants R and F , thus

$$\pi = 2.3026 \frac{RT}{nF} \log a_+ + \pi_0;$$

since R is 1.985 calories, i.e. 1.985×4.184 joules, and F is 96,500 coulombs

$$\begin{aligned} \pi &= \frac{2.3026 \times 1.985 \times 4.184}{n \times 96500} T \log a_+ + \pi_0 \\ &= \frac{0.0001982}{n} T \log a_+ + \pi_0 \quad \dots \quad (\text{xxi}) \end{aligned}$$

At ordinary temperatures (i.e. about 18°C. , 291°K.) the equation may be used in the form

$$\pi = \frac{0.058}{n} \log a_+ + \pi_0 \quad \dots \quad (\text{xxii})$$

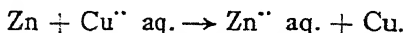
For an electrode material yielding negative ions, e.g. oxygen, chlorine and iodine, the potential becomes more negative with increasing osmotic pressure of the ions; hence the Nernst formula, to include the sign of the potential, should be written:

$$\pi = \frac{RT}{nF} \ln \frac{P}{P'}$$

then

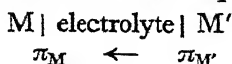
$$\pi = \text{constant} (\pi_0) - \frac{RT}{nF} \ln a_- \quad \dots \quad (\text{xxiii})$$

Nernst Theory of the Galvanic Cell—An insight into the mechanism of a galvanic cell may be obtained on the basis of solution pressures; it will be shown later that the theory is not necessarily rigid and hence the mechanism based on it may be incorrect. As a method of *visualizing* electrode processes, however, the Nernst solution pressure concept has distinct advantages; its limitation must, however, be borne in mind throughout. Suppose a zinc rod is dipped into zinc sulphate and a copper rod into copper sulphate solution, owing to the high solution pressure of the zinc it will send a few ions into solution and leave itself negatively charged; at the same time the copper with its low solution pressure will become positively charged. Double layers will form at each metal and an equilibrium will be reached; neither metal dissolves to any appreciable extent. If the two metals are now connected by a conducting wire and the solutions brought into contact, positive electricity will flow along the wire from the copper to the zinc; the equilibrium at the metal-solution interface is disturbed and more copper ions will deposit on the copper electrode to replace the positive electricity passed along the wire. The flow of positive electricity to the zinc will neutralize its negative charge; thus more zinc will ionize and pass into solution in an attempt to restore the double layer. Hence as long as the two electrodes are connected positive current flows from the copper (positive electrode) through the connecting wire to the zinc (negative electrode); at the same time the latter dissolves and copper is deposited on the former. The chemical reaction occurring, as already indicated, must be



The solution pressure of a metal may alternatively be regarded as its tendency to lose electrons; this is equivalent to the tendency to send off positive ions, since the removal of electrons will result in the formation of these ions. Copper has the lower solution pressure and so will have a smaller tendency than zinc to lose electrons; hence when the zinc and copper electrodes are connected by a wire, electrons will pass from the zinc to the copper along the wire.* At the latter electrode the electrons are removed by copper ions which thus become discharged, whereas at the zinc electrode the withdrawal of electrons leaves zinc ions which pass into solution.

Electromotive Force of a Galvanic Cell—The simplest galvanic cell consists of two electrodes dipping into a liquid thus:



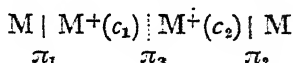
* Note that the flow of electrons, i.e. negative charges, is opposite to that of the 'positive' current.

If electricity passes through this cell in one direction, e.g. right to left, it is observed that the positive charge must pass from metal M' to the electrolyte, but *from* the electrolyte to the metal M . In general, therefore, irrespective of the nature of the metals, one electrode aids the flow of electricity whereas the other opposes it; the *E.M.F.*, or driving force, of the cell must then be represented by the algebraic *difference* of the two separate electrode potentials. A definite convention is necessary when stating the sign of a cell; the European method is to state the potential of the left-hand electrode minus that of the right-hand. Thus in the general cell described

$$E = \pi_M - \pi_{M'}.$$

If $\pi_M > \pi_{M'}$, according to the convention for electrode potentials, then E is positive; current then flows from right to left *through* the cell. When the current flows in the opposite direction $\pi_M < \pi_{M'}$, and the *E.M.F.* of the cell is negative. The American convention is to state the potential of the right-hand electrode first, but as the sign is opposite to that given by the European method the *E.M.F.* of a complete cell has the same sign according to both conventions.

Nernst's Theory of Concentration Cells—The *E.M.F.* of the cell

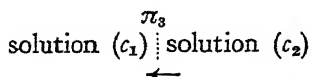


is made up of the potential differences, π_1 and π_2 at the electrode-electrolyte interfaces, and π_3 at the junction of the two solutions. This last potential difference is usually called the **liquid junction potential**, or more simply the **diffusion potential**; the origin and method of evaluation of this potential have been described by Nernst.*

Liquid Junction Potential—When two salt solutions of different concentrations are in contact with one another the more concentrated solution will tend to diffuse into the more dilute; the rate of diffusion of each ion will be roughly proportional to its speed in an electrical field. If the cation moves more rapidly than the anion the former will diffuse ahead of the latter into the dilute solution; this solution will thus become positively charged with respect to the concentrated solution. Should the anion be the faster moving ion the dilute solution will acquire a negative charge. In either case an electrical double layer is produced at the junction of the solutions and the attraction between the opposite charges prevents any appreciable separation of anions from cations. At the junction of two solutions of different concentration there must, therefore, be a potential difference; the magnitude depends

* *Z. physikal. Chem.*, 1888, 2

on the relative speeds of the ions, and its direction is such that the more dilute solution always assumes the charge of the faster moving ion. If the two ions of a binary electrolyte have the same speed there will be no liquid junction potential, since all the ions diffuse at the same rate. The method of calculating the formula for the liquid junction potential is as follows: suppose the concentrations of the two solutions are c_1 and c_2 (activities a_1 and a_2), the more concentrated being on the left-hand side:



If one faraday of electricity passes through the cell from c_2 to c_1 then n_c gm. equiv. of cations are transported from right to left, and n_a gm. equiv. of anions in the opposite direction; n_c and n_a are the transport numbers of the corresponding ions. Let z_+ be the valency of the cations and z_- the valency of the anions, then n_c/z_+ gm. ions of cation are transferred from the solution of ionic concentration c_2 to the one of concentration c_1 , whereas n_a/z_- gm. ions of anion are transferred from c_1 to c_2 . The free energy change involved in this transfer, assuming the transport numbers to remain constant, is given by

$$-\Delta G = \frac{n_c}{z_+} RT \ln \frac{(a_+)_2}{(a_+)_1} + \frac{n_a}{z_-} RT \ln \frac{(a_-)_1}{(a_-)_2}$$

The equivalent electrical work done in moving 1 faraday across the liquid junction at which there is a potential difference of π_3 is $\pi_3 F$; hence

$$\begin{aligned} \pi_3 F &= \frac{n_c}{z_+} RT \ln \frac{(a_+)_2}{(a_+)_1} + \frac{n_a}{z_-} RT \ln \frac{(a_-)_1}{(a_-)_2} \\ \therefore \pi_3 &= \frac{RT}{F} \left\{ \frac{n_c}{z_+} \ln \frac{(a_+)_2}{(a_+)_1} + \frac{n_a}{z_-} \ln \frac{(a_-)_1}{(a_-)_2} \right\} \quad (\text{xxiv}) \end{aligned}$$

This equation gives the value for the liquid junction potential in the most general case.*

Sign of the Liquid Junction Potential—If the value of the junction potential is to be *added* to the conventional potential difference between the electrodes, the result of diffusion must be to cause the flow of positive charges from right to left, or negative from left to right. That is for the diffusion potential to have a conventional positive sign the equation must be positive when $c_1 > c_2$ and the negative ion is the faster, i.e. $n_a > n_c$; negative ions then tend to pass from c_1 to c_2 , that is from left to right. As

* See also, Szabó, *ibid.*, 1935, 174, 22, 33; 1936, 176, 125; Hermans, *ibid.*, 1936, 176, 55, 131; Guggenheim, *Phil. Mag.*, 1936, 22, 983.

written above the equation for π_3 satisfies these requirements for a binary electrolyte, when z_+ and z_- are the same and the activity and concentration ratios are approximately equal; the value obtained in this way may, therefore, be added to the *E.M.F.* of the cell.

E.M.F. of Complete Concentration Cell—According to convention the *E.M.F.* of the complete concentration cell (*E*) will be given by

$$E = \pi_1 + \pi_3 - \pi_2;$$

since $\pi_1 = \pi_0 + \frac{RT}{z_+F} \ln (a_+)_1$ and $\pi_2 = \pi_0 + \frac{RT}{z_+F} \ln (a_+)_2$ *

$$\begin{aligned} E &= \frac{RT}{z_+F} \ln \frac{(a_+)_1}{(a_+)_2} + \frac{RT}{F} \left\{ \frac{n_c}{z_+} \ln \frac{(a_+)_2}{(a_+)_1} + \frac{n_a}{z_-} \ln \frac{(a_-)_1}{(a_-)_2} \right\} \\ &= (1 - n_c) \frac{RT}{z_+F} \ln \frac{(a_+)_1}{(a_+)_2} + n_a \frac{RT}{z_-F} \ln \frac{(a_-)_1}{(a_-)_2} \quad \dots \quad (\text{xxv}) \end{aligned}$$

The mean activity of the salt (*a*) is given by the expression

$$a^v = a_+^{v_+} a_-^{v_-},$$

where v_+ and v_- are the number of cations and anions, respectively, produced by one molecule of electrolyte on ionization, and v is equal to $v_+ + v_-$; since $1 - n_c$ is equal to n_a it follows that

$$E = n_a \frac{RT}{v_+ z_+ F} \ln \frac{a_1}{a_2}, \quad (\text{xxvi})$$

remembering that $v_+ z_+$ is equal to $v_- z_-$. Replacing z_+ , the valency of the reversible ion, by the more usual letter n , equation (xxvi) becomes

$$E = n_a \frac{RT}{v_+ n F} \ln \frac{a_1}{a_2} \quad (\text{xxvii})$$

where a_1 and a_2 are the mean activities of the electrolyte at the concentrations c_1 and c_2 respectively. This equation is identical with the one already deduced on the basis of thermodynamics for the complete *E.M.F.* of a cell with transport (equation xii, p. 292); the method used here, based on the Nernst theory, has the one advantage of dividing up the total *E.M.F.* into its constituent potential differences. The *E.M.F.* of the cell exclusive of the liquid junction potential is $\frac{RT}{nF} \ln \frac{(a_+)_1}{(a_+)_2}$. If the electrolyte is silver nitrate and the electrodes are of silver, n is 1, $v = 2$, $v_+ = 1$, hence

$$E = 2n_a \frac{RT}{F} \ln \frac{a_1}{a_2}.$$

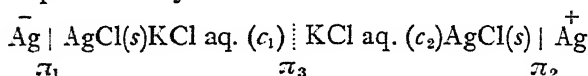
* z_+ is the valency of the positive (reversible) ion.

For the cell $\text{Zn} | \text{ZnCl}_2 \text{ aq. } (c_1) || \text{ZnCl}_2 \text{ aq. } (c_2) | \text{Zn}$, however, n is 2, $r = 3$ and $r_+ = 1$; therefore,

$$E = 3n_a \frac{RT}{2F} \ln \frac{a_1}{a_2}.$$

These equations are not easy to verify experimentally since a_1 and a_2 cannot be determined directly from the concentrations, but an approximate confirmation may be obtained when working with dilute solutions if a_1/a_2 is replaced by c_1/c_2 or by $\alpha_1 c_1/\alpha_2 c_2$, where α is the conductance ratio. Satisfactory agreement with this form of the equation has been obtained by Nernst;* for the cell $\text{Ag} | \text{AgNO}_3 \text{ 0.1N} || \text{AgNO}_3 \text{ 0.01N} | \text{Ag}$, the *E.M.F.* was found to be 0.055 volt at 18°. Taking n_a as 0.527 and $\alpha_1 c_1/\alpha_2 c_2$ as 8.72, the *E.M.F.* of the cell is calculated as 0.057 volt.

Concentration Cells with Reversible Anion Electrodes—
The cell represented by



has electrodes which may be regarded as reversible either with respect to silver ions, or to chlorine ions (see p. 283). The *E.M.F.* may be readily calculated by regarding the electrodes as reversible silver electrodes; as before, provided the conventional formulæ are used, and taking z_+ and z_- as unity,

$$\begin{aligned} E &= \pi_1 + \pi_3 - \pi_2 \\ &= \pi_0 + \frac{RT}{F} \ln (a_{\text{Ag}^+})_1 + \frac{RT}{F} \left\{ n_c \ln \frac{(a_+)_2}{(a_+)_1} + n_a \ln \frac{(a_-)_1}{(a_-)_2} \right\} \\ &\quad - \pi_0 - \frac{RT}{F} \ln (a_{\text{Ag}^+})_2 \end{aligned} \quad (\text{xxviii})$$

where a_+ and a_- refer to potassium and chlorine ions respectively. Since both solutions are saturated with silver chloride, it follows from the activity solubility product principle that

$$(a_{\text{Ag}^+})_1 \times (a_-)_1 = (a_{\text{Ag}^+})_2 \times (a_-)_2.$$

Equation (xxviii) then reduces to

$$E = (1 - n_a) \frac{RT}{F} \ln \frac{(a_-)_2}{(a_-)_1} + n_c \frac{RT}{F} \ln \frac{(a_+)_2}{(a_+)_1}.$$

The mean activity of the potassium chloride, a , is equal to $(a_+ a_-)^{\frac{1}{2}}$; and $1 - n_a$ is equal to n_c ; hence

$$E = 2n_c \frac{RT}{F} \ln \frac{a_2}{a_1} \quad (\text{xxix})$$

* *Z. physikal. Chem.*, 1889, 4, 129; 1891, 7, 477; see also Abegg and Cumming, *Z. Elektrochem.*, 1907, 13, 18.

where a_1 and a_2 are the activities of the potassium chloride at concentrations c_1 and c_2 respectively. Introducing activity coefficients,

$$E = 2n_c \frac{RT}{F} \ln \frac{\gamma_2 c_2}{\gamma_1 c_1} \quad . \quad . \quad . \quad (xxx)$$

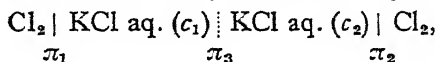
or if γ_2/γ_1 is assumed to be approximately equal to α_2/α_1 , where α_1 and α_2 are the conductance ratios,

$$E = 2n_c \frac{RT}{F} \ln \frac{\alpha_2 c_2}{\alpha_1 c_1} \quad (xxx_i)$$

For any cell of this type the general formula may be deduced either by the thermodynamic method or by the method involving the separate electrode and junction potentials ; thus

$$E = n_c \frac{v}{v-n} \frac{RT}{F} \ln \frac{a_2}{a_1}, \quad . \quad . \quad . \quad (xxxii)$$

where n is the valency of the anions. This equation differs from that for a cell reversible with respect to cations in two aspects ; n_c replaces n_a , and a_2/a_1 appears instead of a_1/a_2 . This indicates that the sign of the *E.M.F.* is reversed ; the electrode in the more concentrated potassium chloride solution is negative, as is to be expected for an electrode reversible with respect to negative ions.* The *E.M.F.* of the cell can easily be deduced by considering it as :

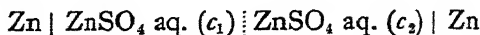


since $\pi_1 = \pi_0 - \frac{RT}{F} \ln (a_-)_1$, and $\pi_2 = \pi_0 - \frac{RT}{F} \ln (a_-)_2$

and π_3 has the same value as before. This is in fact the simplest method for deducing the general equation (xxxii). The *E.M.F.* due to the electrodes alone is

$$- \frac{RT}{nF} \ln \frac{(a_-)_1}{(a_-)_2}.$$

Measurement of Liquid Junction Potential—A method for measuring the potential difference at the interface between two solutions of zinc sulphate was devised by Cohen and Tombrock ; † the same principle may, however, be applied to other solutions. In the two cells



and $\text{Hg} | \text{Hg}_2\text{SO}_4(s) | \text{ZnSO}_4 \text{ aq. } (c_1) : \text{ZnSO}_4 \text{ aq. } (c_2) | \text{Hg}_2\text{SO}_4(s) | \text{Hg},$

* It may be mentioned, too, that the more concentrated chloride solution will have the smaller silver ion concentration, and so the metallic silver immersed in it will have the more negative potential.

† *Z. Elektrochem.*, 1907, 13, 612.

the liquid junction potentials (π_3) are identical both in magnitude and direction, but the potentials due to the electrodes although equal act in opposite directions. Thus, assuming the activities of the zinc and sulphate ions are equal,

$$E_1 = \frac{RT}{2F} \ln \frac{a_1}{a_2} + \pi_3$$

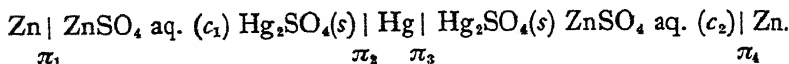
$$\text{and} \quad E_2 = \frac{RT}{2F} \ln \frac{a_2}{a_1} + \pi_3$$

$$\text{On adding} \quad E_1 + E_2 = 2\pi_3$$

$$\text{or} \quad \pi_3 = \frac{E_1 + E_2}{2} \quad (\text{xxxiii})$$

By measuring E_1 and E_2 , the value of π_3 may be determined. Even though liquid junction potentials can be calculated or measured, it is always assumed that a sharp boundary exists between the two solutions. In practice diffusion and mixing of the solutions occur, and the actual junction potential may be quite different from the calculated value. For many purposes it is desirable to eliminate the junction potential entirely; the methods by means of which this may be achieved will be considered later.

Concentration Cells without Transport—The *E.M.F.*'s of such cells may be calculated on the basis of the Nernst theory; consider the example studied previously on a purely thermodynamic basis :



There are no liquid junctions but four metal-liquid potentials; the *E.M.F.* of the cell is given by

$$E = \pi_1 - \pi_2 + \pi_3 - \pi_4,$$

since the cell is equivalent to the two cells $(\pi_1 - \pi_2)$ and $(\pi_3 - \pi_4)$ acting in conjunction. Now

$$\pi_1 - \pi_4 = \frac{RT}{2F} \ln \frac{(a_+)_1}{(a_+)_2}$$

$$\text{and} \quad \pi_3 - \pi_2 = \frac{RT}{2F} \ln \frac{(a_{\text{Hg}})_2}{(a_{\text{Hg}})_1} = \frac{RT}{2F} \ln \frac{(a_-)_1}{(a_-)_2}^*$$

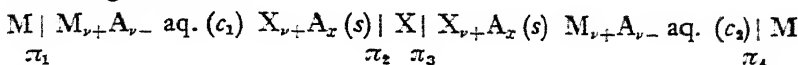
* The terms $(a_{\text{Hg}})_1$ and $(a_{\text{Hg}})_2$ represent the activities of mercurous ions (Hg_2^{2+}) in the zinc sulphate solutions c_1 and c_2 respectively; by the activity product principle $(a_{\text{Hg}})_1 \times (a_-)_1 = (a_{\text{Hg}})_2 \times (a_-)_2$, and so

$$(a_{\text{Hg}})_2 / (a_{\text{Hg}})_1 = (a_-)_1 / (a_-)_2.$$

where a_+ and a_- refer to the Zn^{++} and SO_4^{--} ions respectively; hence

$$\begin{aligned} E &= \frac{RT}{2F} \ln \frac{(a_+)_1}{(a_+)_2} + \frac{RT}{2F} \ln \frac{(a_-)_1}{(a_-)_2} \\ &= \frac{RT}{F} \ln \frac{a_1}{a_2} \end{aligned} \quad (\text{xxxiv})$$

For the general cell



where $\text{X}_{\nu_+} \text{A}_x$ is an insoluble salt of the metal X of valency x ; the valencies of M and A are ν_+ and ν_- , and these are equal to ν_- and ν_+ respectively. Since

$$E = \pi_1 - \pi_2 + \pi_3 - \pi_4$$

$$\text{and} \quad \pi_1 - \pi_4 = \frac{RT}{\nu_+ F} \ln \frac{(a_+)_1}{(a_+)_2} = \frac{RT}{\nu_- F} \ln \frac{(a_-)_1}{(a_-)_2}$$

$$\text{and} \quad \pi_3 - \pi_2 = \frac{RT}{x F} \ln \frac{(a_x)_2}{(a_x)_1} = \frac{RT}{\nu_+ F} \ln \frac{(a_-)_1}{(a_-)_2} *$$

$$\begin{aligned} \therefore E &= \frac{RT}{F} \left\{ \frac{1}{\nu_-} \ln \frac{(a_+)_1}{(a_+)_2} + \frac{1}{\nu_+} \ln \frac{(a_-)_1}{(a_-)_2} \right\} \\ &= \frac{\nu_+ + \nu_-}{\nu_+ \nu_-} \cdot \frac{RT}{F} \ln \frac{a_1}{a_2} \\ &= \frac{\nu}{\nu_+ n F} \ln \frac{a_1}{a_2} \end{aligned} \quad (\text{xxxv})$$

where $\nu_+ + \nu_-$ is replaced by ν , and ν_- , the valency of the reversible ion M, by n . For a cell in which the outside electrodes are reversible with respect to the anion,

$$E = \frac{\nu}{\nu_- n F} \ln \frac{a_2}{a_1} \quad (\text{xxxvi})$$

where n is the valency of the anion; the sign of the cell is reversed. Cells of the type

$\text{Ag} | \text{AgCl}(s) | \text{KCl aq. } (c_1) | \text{K} | \text{KCl aq. } (c_2) | \text{AgCl}(s) | \text{Ag}$
were studied by MacInnes and others;† the *E.M.F.* is given by

$$E = \frac{2RT}{F} \ln \frac{a_2}{a_1}.$$

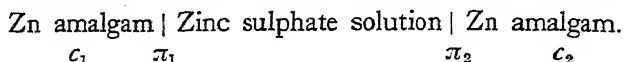
Types of Concentration Cells—Reversible concentration cells may be divided into two main categories: (i) those in which

* By the solubility product principle $(a_x)^{\nu_+} (a_-)^x = \text{constant}$; therefore $(a_x)_1 / (a_x)_2 = \{(a_-)_2 / (a_-)_1\}^{x/\nu_+}$.

† *J. Amer. Chem. Soc.*, 1915, 37, 1445; see also references on p. 365 *infra*.

the concentration (i.e. activity) of the ions is kept constant and the activity of the electrode varied; and (ii) those in which two identical electrodes are used in solutions of varying ion activity. Some cells of the latter type have been discussed and reference will be made to others subsequently; in the meantime examples of the former type will be described.

Amalgam Cells—A concentration cell may be made up with electrodes of two amalgams containing the same base metal, e.g. zinc, dissolved in mercury at different concentrations; the electrolyte is a solution of the salt of the metal, e.g. zinc sulphate, thus:



If P_1 and P_2 are the solution pressures of zinc in the two amalgams, and P is the osmotic pressure of zinc ions in the solution, then

$$\begin{aligned} E = \pi_1 - \pi_2 &= \frac{RT}{2F} \ln \frac{P}{P_1} - \frac{RT}{2F} \ln \frac{P}{P_2} \\ &= \frac{RT}{2F} \ln \frac{P_2}{P_1} \end{aligned} \quad (\text{xxxvii})$$

The more concentrated amalgam probably has the higher solution pressure and so forms the more negative electrode, in agreement with the formula. The exact connection between solution pressure and concentration is not obvious and so the equation cannot be developed further; another method of treatment is, however, available. Consider the passage of nF coulombs through the cell as a result of connecting together the two electrodes; 1 gm. atom of zinc will dissolve from the more concentrated (negative) amalgam and an equal amount will be deposited on the more dilute amalgam. The net result is the transfer of 1 gm. atom of zinc from amalgam of concentration c_1 (activity a_1) to the amalgam of concentration c_2 (activity a_2), and the free energy change involved in this process is

$$-\Delta G = \frac{1}{m} RT \ln \frac{a_1}{a_2}$$

where m is the number of atoms of zinc per molecule when dissolved in the mercury. The equivalent amount of electrical work is nFE , where E is the *E.M.F.* of the cell; hence

$$nFE = \frac{1}{m} RT \ln \frac{a_1}{a_2}$$

$$\text{and} \quad E = \frac{RT}{mnF} \ln \frac{a_1}{a_2} \quad . \quad . \quad (\text{xxxviii})$$

For zinc and copper amalgams $m = 1$ and $n = 2$, and so

$$E = \frac{RT}{2F} \ln \frac{a_1}{a_2}$$

Since the activities of the amalgams cannot be determined easily, the ratio a_1/a_2 is generally replaced by c_1/c_2 and in the resulting form the equation was first deduced by Türlin* and verified by Meyer.† Although the equation was reasonably satisfactory for zinc, lead, tin, copper and cadmium amalgams it failed when applied to amalgams of alkali and alkaline-earth metals; ‡ Cady suggested that the concentration of the amalgam did not represent its real activity and that the equation for the *E.M.F.* should be written

$$E = \frac{RT}{mnF} \ln \frac{c_1}{c_2} + \frac{U}{nF} \quad . \quad . \quad . \quad (\text{xxxix})$$

where U represents, in joules, the heat of dilution of the amalgam c_1 to c_2 .§ This formula is in better agreement with observed results than the simple equation, but compound formation between the dissolved metal and the mercury is also a factor which causes deviations from both ideal and Cady formulæ.||

Electrodes in Different Physical Condition—The solution pressure of a metal depends on its physical condition (p. 295); hence 'concentration cells' may be set up with two electrodes of the same metal provided there is some difference between them. The electrodes may be of large and small crystals respectively, or of strained and unstrained metal; cells with electrodes of this type are probably responsible to some extent for the corrosion of metals (see p. 504). Cells involving two allotropic forms of a metal, e.g. tin, have been used to determine the transition temperature of these forms (p. 373).

Gravity Cells—This type of concentration cell was devised by Des Coudres; ** it consists of two mercury electrodes dipping into a mercurous salt solution. The electrodes consist of a short column and a long column of mercury, placed in tubes closed with parchment membranes which retain the mercury but allow the

* *Z. physikal. Chem.*, 1890, 5, 340; see also Bancroft, *J. Physical Chem.*, 1899, 3, 107.

† *Ann. Physik*, 1890, 40, 244; *Z. physikal. Chem.*, 1891, 7, 447.

‡ Cady, *J. Physical Chem.*, 1898, 2, 551.

§ The quantity Cady actually intended was not heat of dilution, but the heat of transfer of 1 gm. molecule of metal from one amalgam to the other; the latter is equal to the difference between the heats of solution at the two concentrations; see Richards (T. W.) and Daniels, *J. Amer. Chem. Soc.*, 1919, 41, 1732; Anderson, *ibid.*, 1926, 48, 2285.

|| Richards (T. W.) and Conant, *ibid.*, 1922, 44, 601; Anderson, *loc. cit.*; Bent and Gilfillan, *ibid.*, 1933, 55, 3989.

** *Ann. Physik*, 1892, 46, 292.

passage of ions. The mercury in the longer column is at a higher pressure, and so has a greater free energy content and a larger solution pressure than the other; this electrode thus becomes negative with respect to the other. Mercury dissolves from the negative electrode and is deposited on the positive so that the levels tend to equalize. The electrical energy produced in the cell for the passage of 1 faraday is equal to the gravitational work obtainable by lowering 1 gm. equiv. of mercury (200 gms.) from the top of the long to the top of the shorter column, i.e. through a height h cms.; this mechanical work is equal to $h \times 200 \times g$ ergs (where g , the acceleration due to gravity, is 981 cms. per sec. per sec.) or $200 \times 10^{-7} \times hg$ joules. The equivalent amount of electrical work is FE , where E is the *E.M.F.* of the cell and F is 96,500 coulombs; hence

$$E = \frac{h \times 981 \times 200 \times 10^{-7}}{96500} \text{ volt} \quad (\text{xl})$$

$$= 2.03 \times 10^{-7} h \text{ volt.}$$

The *E.M.F.* of such cells as measured by Des Coudres and as calculated from this equation are given in Table XLIII.

TABLE XLIII

OBSERVED AND CALCULATED *E.M.F.*'s OF GRAVITY CELLS

h		E (calcd.).	E (obsd.).
36 cm.	.	7.2×10^{-6} volt	7.4×10^{-6} volt
46 "	.	9.3×10^{-6}	10.5×10^{-6}
113 "	.	22.9×10^{-6}	21.0×10^{-6}

The agreement is good, perhaps better than would be expected in view of the fact that the membranes used for holding up the mercury probably introduce a potential difference into the cell.* It is interesting to note that since gravitational energy is all 'free energy' and does not vary with temperature, the temperature coefficient of a gravity cell is zero; allowance must, however, be made for expansion.†

Gas Cells.†—Hydrogen Electrodes—Just as a metal in contact with a solution of its ions constitutes a reversible electrode, so it is possible to have such an electrode consisting of hydrogen and a solution of hydrogen ions. On account of the gaseous nature of hydrogen a special device is used in order to render measurable

* Cf. Ort and France, *J. Physical Chem.*, 1929, 33, 801.

† See also Tolman, *Proc. Amer. Acad. Arts Sci.*, 1910, 46, 5, for other gravity cells.

‡ For early work on gas electrodes see Grove, *Phil. Mag.*, 1839, 14, 129; Beetz, *Ann. Physik*, 1849, 77, 493; 1853, 90, 42; Ostwald, *Z. physikal. Chem.*, 1893, 11, 521; Smale, *ibid.*, 1894, 14, 577.

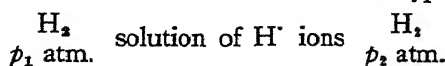
the potential difference between gas and solution. The method adopted is to place a small sheet of platinized platinum so that it is partly immersed in the solution and partly surrounded by gas; a type of hydrogen electrode vessel is shown in Fig. 21.* The platinized platinum adsorbs hydrogen and behaves as if it were a solid electrode of the gas; it allows the change from gaseous to ionic states and the reverse process to occur without any hindrance. The electrode is truly reversible and attains a potential dependent only on the pressure of the gas and the activity of the hydrogen ions in the electrolyte. The platinized platinum may be replaced by a gold electrode covered with iridium or palladium black without affecting the potential. If hydrogen atoms pass into solution as positive ions they transfer their electrons to the metal electrode which thus acquires a negative charge; if the ions are discharged they take electrons from the metal and leave it positively charged. The potential difference between the metal and solution may then be expressed by the ordinary Nernst formula

$$\pi = \frac{RT}{nF} \ln \frac{P}{\bar{P}}$$

where n is unity, P is the osmotic pressure of the ions and \bar{P} the solution pressure of the gas. Alternatively the formula, for a constant pressure of hydrogen gas, may be written:

$$\pi = \pi_0 + \frac{RT}{F} \ln a_{H^+} \quad . \quad . \quad . \quad (xli)$$

where a_{H^+} is the activity of hydrogen ions in the solution. Since the value of \bar{P} will undoubtedly depend on the gas pressure, there may be constructed a concentration cell of the type:



where p_1 and p_2 are different pressures of hydrogen, P_1 and P_2 ,

* For other types of electrode vessel and further practical details, see p. 376.

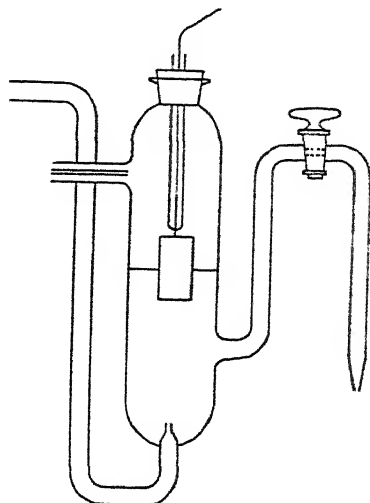


FIG. 21.—Gas-electrode vessel

being the corresponding solution pressures. From the Nernst equation the *E.M.F.* (*E*) may be deduced as

$$E = \frac{RT}{F} \ln \frac{P_2}{P_1} \quad \dots \quad (\text{xlii})$$

The hydrogen at the higher pressure forms the negative electrode. During the production of current by this cell hydrogen dissolves at the electrode with the higher pressure (p_1) and is deposited at the electrode of lower pressure (p_2); the passage of two faradays results in the transfer of 2 gm. atoms, i.e. 1 gm. mol., of hydrogen gas, and the free energy change may be written as equal to $RT \ln p_1/p_2$, if the gas laws are obeyed. The electrical work done during the transfer is $2EF$, and so

$$E = \frac{RT}{2F} \ln \frac{p_1}{p_2} \quad (\text{xliii})$$

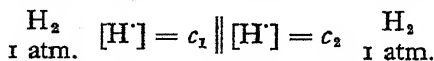
This equation connecting the *E.M.F.* with the gas pressure has been confirmed over a range of pressures from 0.005 to 400 atmospheres; at higher pressures deviations occur as the departure of hydrogen from the ideal gas law behaviour is quite appreciable.* The connection between gas pressure and solution pressure is seen by comparing equations (xlii) and (xliii), reversing the latter to allow for the sign; thus

$$\frac{P_1}{P_2} = \sqrt{\frac{p_1}{p_2}} \quad \dots \quad (\text{xliv})$$

That is, the solution pressure is directly proportional to the square root of the gas pressure of hydrogen.

A gas electrode in which the hydrogen is replaced by its isotope deuterium has been studied in a limited number of cases; its potential is 0.0034 volt more negative than that of the ordinary hydrogen electrode at the same (atmospheric) pressure.† Concentration cells involving other gases, e.g. oxygen and chlorine, at different pressures, may also be obtained; reference to these will be made later (p. 333).

In addition to cells involving different electrode activities, gas cells are possible in which the gas is at the same pressure in both electrodes but the latter dip into solutions of different ion activities; thus



* Loomis and Acree, *J. Amer. Chem. Soc.*, 1916, **38**, 2391; Loomis, Acree and Myers, *J. Physical Chem.*, 1917, **21**, 334; Hainsworth and MacInnes, *J. Amer. Chem. Soc.*, 1922, **44**, 1021; Hainsworth, Rowley and MacInnes, *ibid.*, 1924, **46**, 1437; Tammann and Dieckmann, *Z. anorg. Chem.*, 1926, **150**, 129; Romann and Chang, *Bull. Soc. chim.*, 1932, **51**, 932.

† Abel, Bratu and Redlich, *Z. physikal. Chem.*, 1935, **173**, 353.

The *E.M.F.* of this cell, apart from diffusion potential, is given by

$$E = \frac{RT}{F} \ln \frac{(a_{H^+})_1}{(a_{H^+})_2} \quad \dots \dots \dots (xlv)$$

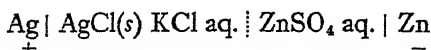
where $(a_{H^+})_1$ and $(a_{H^+})_2$ are the hydrogen ion activities in the two solutions. Similar cells with oxygen and chlorine are possible.

One characteristic should be observed of all concentration cells; when they produce current the different concentrations, or activities, tend to equalize one another. Thus, the more dilute solutions always increase in concentration and vice versa; the more concentrated amalgam loses its metal to the less concentrated, and gas is transferred from the electrode at higher pressure to the one at lower pressure. In every case the *E.M.F.* of the cell decreases whilst working and eventually becomes zero when the activities become equal.

CHAPTER XIII

REVERSIBLE CELLS—II

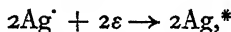
CHEMICAL Cells—There are a large number of galvanic cells of which the Daniell cell is a type ; they obtain their energy as a result of the transformation of chemical energy. Any cell consisting of two electrodes reversible with respect to different ions is a reversible chemical cell to which the Gibbs-Helmholtz equation is applicable. A few examples will be considered here. In the cell



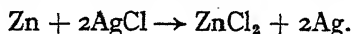
the zinc electrode is negative and hence dissolves as ions ; at the other electrode silver is deposited from solution leaving a corresponding amount of chlorine ions derived from silver chloride. Thus

At the negative electrode : $\text{Zn} \rightarrow \text{Zn}^{++} + 2\varepsilon.$

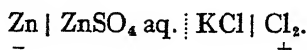
At the positive electrode : $2\text{AgCl} \rightarrow 2\text{Ag}^+ + 2\text{Cl}'$



and the net reaction for the passage of *two* faradays, is



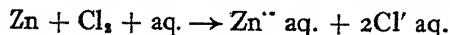
The product of the *E.M.F.* of this cell and $2F$ coulombs gives the free energy of this reaction in joules. One or both of the electrodes may be gas electrodes, thus



At the negative electrode : $\text{Zn} \rightarrow \text{Zn}^{++} + 2\varepsilon.$

At the positive electrode : $\text{Cl}_2 + 2\varepsilon \rightarrow 2\text{Cl}',$

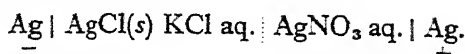
and the net reaction for the passage of two faradays is



In another type of chemical cell the two electrodes are reversible with respect to the same ions ; such cells may be considered as concentration cells, but strictly speaking they are chemical cells as

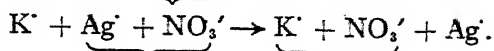
* The symbol ε is used to represent an electron.

the electrical energy is produced as the result of a chemical action. Consider the cell



At the negative electrode : $\text{Ag} \rightarrow \text{Ag}' + \varepsilon ;$

in the solution : $\text{Ag}' + \text{K}' + \text{Cl}' \rightarrow \text{AgCl} + \text{K}'$

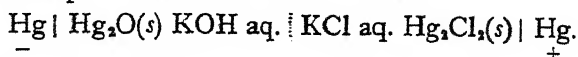


At the positive electrode : $\text{Ag}' + \varepsilon \rightarrow \text{Ag},$

and the total reaction is $\text{AgNO}_3 + \text{KCl} \rightarrow \text{AgCl} + \text{KNO}_3,$

or ionically $\text{Ag}' + \text{Cl}' \rightarrow \text{AgCl}$ for 1 faraday.

Another example of the same kind of cell is



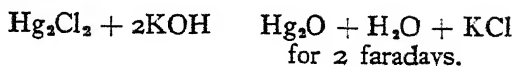
At the negative electrode : $2\text{Hg} \rightarrow \text{Hg}_2'' + 2\varepsilon ;$

in the solution : $\text{Hg}_2'' + 2\text{K}' + 2\text{OH}' \rightarrow \text{Hg}_2\text{O} + \text{H}_2\text{O} + 2\text{K}',$

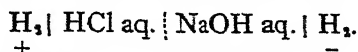
then $\text{Hg}_2\text{Cl}_2 \cdot \text{Hg}_2'' + 2\text{Cl}'.$

At the positive electrode : $\text{Hg}_2'' + 2\varepsilon \rightarrow 2\text{Hg},$

and the complete reaction is

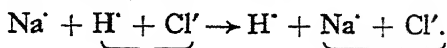


An important chemical cell is one involving two hydrogen electrodes immersed in acid and alkaline solutions respectively ; thus



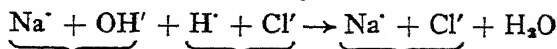
At the negative electrode : $\text{H} \rightarrow \text{H}' + \varepsilon ;$

in the solution : $\text{H}' + \text{Na}' + \text{OH}' \rightarrow \text{H}_2\text{O} + \text{Na}'$



At the positive electrode : $\text{H}' + \varepsilon \rightarrow \text{H}$

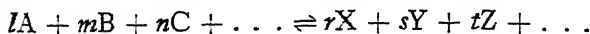
Hence for the passage of 1 faraday the reaction is



or simply $\text{OH}' + \text{H}' \rightarrow \text{H}_2\text{O}.$

The actual reaction is thus the neutralization of acid and alkali. It must be mentioned that the *E.M.F.* of a chemical cell depends on the activities of the reacting species ; this must be so in accordance with thermodynamic requirements, since the free energy of a

process depends on the activities of both reactants and resultants. By the van 't Hoff isotherm, for any reversible process

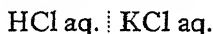


the change of free energy is given by

$$-\Delta G = RT \ln K - RT \ln \frac{a_X^r \cdot a_Y^s \cdot a_Z^t \cdot \dots}{a_A^l \cdot a_B^m \cdot a_C^n \cdot \dots}$$

where K is the equilibrium constant, and the a terms are the arbitrary activities. If this reaction occurs for the passage of n faradays in a reversible cell of *E.M.F.* equal to E , then $-\Delta G = nFE$ joules; the a terms are now the activities of the various reactants and resultants *in the cell*.

Liquid Junctions—The potential difference at a junction consisting of two solutions of the same electrolyte has been considered, but in chemical cells two different electrolytes are involved. As in the case of identical electrolytes the sign of the potential depends on the speeds of the various ions present, although with many junctions it is not possible to tell by inspection in which direction the potential will act. For the simple junction



it is clear that the acid solution will be negative because the hydrogen ion moves so much more rapidly than does the potassium ion; similarly alkaline solutions will generally be positively charged on account of the high velocity of the hydroxyl ion.

A formula for the magnitude of the diffusion potential between two dissimilar electrolytes was first deduced thermodynamically by Planck,* on the assumption that the boundary is initially sharp; the expression, when all the ions have the same valency n , is:

$$\pi_d = \frac{RT}{nF} \ln \xi$$

where the quantity ξ is defined by the equation:

$$\frac{\xi u_1 c_1 - u_2 c_2}{v_1 c_1 - \xi v_2 c_2} \ln \frac{c_1}{\xi c_1 - c_2} + \ln \frac{c_1}{\xi c_1 - \xi c_2} \quad (\text{xlv})$$

In this equation c_1 and c_2 are the sum of the concentrations of anions and cations in the two solutions, u_1 and u_2 are the mobilities of the two cations, and v_1 and v_2 those of the anions at infinite dilution. The equation is limited, strictly, to dilute solutions and to a boundary which is sharper than can be realized experimentally.

* *Ann. Physik*, 1890, 40, 561.

Fales and Vosburgh* have tested the Planck formula by measuring the junction potential between solutions of potassium chloride and hydrochloric acid, viz.

α -Molar KCl : 1.0 N-HCl, and 0.1 N-HCl

where α ranged from 0.1 to 4.1. The agreement between the experimental and calculated values was not good, except for the more dilute solutions. The potential between 4.1N-KCl and 0.1N-HCl was found to be negligible, but the formula indicated a value of 0.005 volt. The Planck equation has been extended by Johnson† to include cases in which the ions have different valencies.

Henderson‡ has assumed that the connecting boundary between two solutions consists of a series of mixtures of electrolytes in all proportions; this is probably much nearer to the actual behaviour than the sharp boundary assumed by Planck.§ The formula derived on these grounds, for any number of dissolved electrolytes, is

$$\pi_d = \frac{RT}{F} \frac{(U_1 - V_1) - (U_2 - V_2)}{(U_1' + V_1') - (U_2' + V_2')} \ln \frac{U_1' + V_1'}{U_2' + V_2'}, \quad (\text{xlvi})$$

where in one solution :

$$\begin{aligned} U_1 &= u_1c_1 + u_2c_2 + u_3c_3 + \dots \\ V_1 &= v_1c_1 + v_2c_2 + v_3c_3 + \dots \\ U_1' &= u_1n_1c_1 + u_2n_2c_2 + u_3n_3c_3 + \dots \\ V_1' &= v_1n_1c_1 + v_2n_2c_2 + v_3n_3c_3 + \dots \end{aligned}$$

and the corresponding quantities in the second solution are represented by U_2 , V_2 , U_2' and V_2' . This gives the general equation for the potential difference between two solutions each of which may contain different ions at various valencies n . The Henderson equation appears to give results in general agreement with those obtained experimentally.||

A special case may be considered when the cations, for example, in both solutions are identical and their total concentrations are

* *J. Amer. Chem. Soc.*, 1918, 40, 1291.

† *Ann. Physik*, 1904, 14, 995; also see Pleyel, *Z. physikal. Chem.*, 1910, 72, 1; Denina, *Gazz.*, 1926, 56, 798.

‡ *Z. physikal. Chem.*, 1907, 59, 118; 1908, 63, 325.

§ Bjerrum, *Z. Elektrochem.*, 1911, 17, 58; Cumming and Gilchrist, *Trans. Faraday Soc.*, 1913, 9, 174; Guggenheim, *J. Amer. Chem. Soc.*, 1930, 52, 1315.

|| For discussion of the relative merits of the Planck and Henderson formulæ, see Plettig, *Ann. Physik*, 1930, 5, 735; Planck, *Sitzungsber. preuss. Akad. Wiss.*, 1930, 367; 1931, 113; 1933, 3; Chang, *Ann. Physik*, 1933, 16, 513; Sitte, *Z. Physik*, 1934, 91, 622, 642, 651; 1935, 93, 698; Planck, *ibid.*, p. 696.

the same in both solutions; the Planck and Henderson formulæ each reduce to the expression

$$\pi_d = \frac{RT}{nF} \ln \frac{u + v_1}{u + v_2}.$$

If the anions, instead of the cations, are the same

$$\pi_d = \frac{RT}{nF} \ln \frac{u_1 + v}{u_2 + v}.$$

These formulæ have been put into the form

$$\pi_d = \frac{RT}{nF} \ln \frac{\Lambda_1}{\Lambda_2} \quad (\text{xlviii})$$

by Lewis and Sargent,* the equivalent conductances being the actual values for the solutions considered, and not for infinite dilution, as implied in the Planck and Henderson equations. The Lewis and Sargent formula, although of limited applicability, is claimed to give results in agreement with observation.

A similar modification of the Henderson formula has been made by Cumming;† the values of u and v used are those at the actual concentration of the solutions, and not at infinite dilution. If n_1 is the valency of both ions in the first solution, n_2 that of the ions in the second solution, and n_{c_1} and n_{c_2} the corresponding cation transport numbers in those solutions, then

$$\pi_d = \frac{RT}{F} \cdot \frac{\kappa_1(2n_{c_1} - 1) - \kappa_2(2n_{c_2} - 1)}{\kappa_1 n_1 - \kappa_2 n_2} \ln \frac{\kappa_1 n_1}{\kappa_2 n_2} \quad (\text{xlix})$$

where κ_1 and κ_2 are the specific conductances. The differences between observed and calculated values are of the order of 1–2 millivolts. It is probable that the introduction of activities, instead of concentrations, into the Henderson formula would give better agreement with experimental observations,‡ but the individual ion activities required for this purpose cannot be determined experimentally (cf. p. 368).

Elimination of Liquid Junction Potentials.§—Since the

* *J. Amer. Chem. Soc.*, 1909, **31**, 363; see MacInnes and Yeh, *ibid.*, 1921, **43**, 2563. For an alternative approach, see Martin (F. D.) and Newton, *J. Physical Chem.*, 1935, **39**, 485.

† *Trans. Faraday Soc.*, 1912, **8**, 86.

‡ Büchi, *Z. Elektrochem.*, 1924, **30**, 443; Taylor (P. B.), *J. Physical Chem.*, 1927, **31**, 1478. For other aspects of liquid junction potentials see Brønsted, *J. Amer. Chem. Soc.*, 1922, **44**, 877; MacInnes and Jones (P. T.), *ibid.*, 1926, **48**, 2834; Harned, *J. Physical Chem.*, 1926, **30**, 433; Guggenheim, *ibid.*, 1929, **33**, 842; 1930, **34**, 1540, 1758; Chloupek *et al.*, *Coll. Czech. Chem. Comm.*, 1933, **5**, 469, 527; Čupr, *J. Chim. physique*, 1934, **31**, 326; see also references on p. 300 *supra*.

§ When liquid junction potentials are eliminated a double line is used in symbolizing the cell, thus HCl aq. || NaCl aq.

value of the potential cannot be calculated with any accuracy, except perhaps in the limited case covered by the Lewis and Sargent formula, it is advisable to eliminate the liquid junction potential if possible. The magnitude of this potential may be realized from the values quoted in Table XLIV which have been obtained from the literature.

TABLE XLIV

LIQUID JUNCTION POTENTIALS (EXPERIMENTAL VALUES)

0.1N-HCl	0.1N-KCl	0.028 volt
"	0.05N-KCl	0.053
"	0.1N-LiCl	0.035
"	0.05N-LiCl	0.058
"	0.01N-LiCl	0.091
0.01N-HCl	0.1N-KCl	0.010
0.1N-NaCl	0.1N-KCl	0.005
0.2N-KCl	0.2N-KBr	0.0004
0.2N-NaCl	0.2N-NaOH	0.019

In order to eliminate the junction potential Nernst* suggested the device of adding an indifferent electrolyte (e.g. KCl or KNO_3) at the same concentration to both sides of the cell; if the concentration of this added substance is much greater than that of any other electrolyte present the former will carry almost all the current. Since its concentration is the same on both sides of the boundary of the two half-elements it will produce no potential difference at the junction. This method of eliminating the diffusion potential is of limited application, chiefly because the addition of an excess of electrolyte will have a marked effect on the activities of the reversible ions; the error introduced in this way may be considerable. A more satisfactory method is to place a concentrated solution of potassium chloride or of ammonium nitrate—a 'salt-bridge'—between the solutions in the two half-cells.† Measurements have shown that the liquid junction potential may be considerably reduced by the insertion of a suitable salt-bridge. Fales and Vosburgh‡ consider that there is no contact potential between 4.1N-potassium chloride solution and 0.1 to 0.01N-hydrochloric acid; hence the concentrated salt solution is able to eliminate the high potential which would be expected from the presence of the

* See Bugarsky, *Z. anorg. Chem.*, 1897, **14**, 145.

† Tower, *Z. physikal. Chem.*, 1896, **20**, 198; Bjerrum, *ibid.*, 1905, **53**, 428; Cumming and Abegg, *Z. Elektrochem.*, 1907, **13**, 17; Cumming, *Trans. Faraday Soc.*, 1907, **2**, 213; Buckley and Hartley (*Phil. Mag.*, 1929, **8**, 320) used sodium iodide in methyl alcohol solution, and Partington and Simpson (*Trans. Faraday Soc.*, 1930, **26**, 625) employed potassium thiocyanate in ethyl alcohol, when studying cells involving these solvents.

‡ *loc. cit.*; see also, Kline, Meacham and Acree, *Bur. Stand. J. Res.*, 1932, **8**, 101.

rapidly moving hydrogen ion. In most work where it is desirable to eliminate the liquid junction potential a bridge of saturated potassium chloride is used, although there is some doubt if this is always completely effective.*

The efficacy of potassium chloride and ammonium nitrate in eliminating diffusion potential is probably connected with the fact that in these salts the anion and cation transport numbers are almost identical; this has led Takegami† to devise mixtures in which the average mobilities of anions and cations are exactly equal. Saturated solutions of such mixtures, e.g. 89.93 gm. mols. ammonium nitrate to 10.07 gm. mols. lithium chloride, and 81.87 gm. mols. potassium chloride to 18.13 gm. mols. potassium nitrate, have been stated to be very satisfactory for eliminating junction potentials. In addition to the salts mentioned the use of sodium nitrate and lithium acetate has also been proposed.‡ A method which combines the partial elimination of the potential with an extrapolation has been suggested by Bjerrum;§ it is assumed that the introduction of 3.5*N*-potassium chloride as a salt-bridge eliminates twice as much of the diffusion potential as does a 1.75*N*-solution. Thus, if E is the *E.M.F.* of a cell when the junction potential is eliminated, $E_{3.5}$ the value when a 3.5*N*-solution of potassium chloride is used as intermediate liquid, and $E_{1.75}$ the value when a 1.75*N*-solution is used, then

$$E_{3.5} - E = \frac{1}{2}(E_{1.75} - E).$$

Since $E_{3.5}$ and $E_{1.75}$ can be measured, E may be calculated. Aten and van Dalfsen|| favour this method as it indicates the magnitude of the correction.

Reproducible Liquid Junctions—In many *E.M.F.* studies the liquid junction potential is included in the measurement, and even if it is not possible to calculate its value, and so make allowance for it, it is always essential that the boundary should be definite and reproducible. As a rule the boundary changes with time as a result of diffusion,** and one formed at the tip of a tube is particularly unstable. Bjerrum†† suggested bringing the two liquids together in a U-tube containing sand; the efficiency of this method is, however, disputed.‡‡ The use of a membrane, e.g. parchment

* Scatchard, *J. Amer. Chem. Soc.*, 1925, 47, 696.

† *Mem. Coll. Sci. Kyoto*, 1924, 7, 45.

‡ Drucker *et al.*, *Z. physikal. Chem.*, 1927 125, 394.

§ *Ibid.*, 1905, 53, 428. || *Rec. trav. chim.*, 1926, 45, 177.

** Walpole, *J. Chem. Soc.*, 1914, 105, 2501; Fales and Vosburgh, *loc. cit.*

†† *Z. Elektrochem.*, 1911, 17, 389.

‡‡ Myers and Acree, *Amer. Chem. J.*, 1913, 50, 396; Lewis, Brighton and Sebastian, *J. Amer. Chem. Soc.*, 1917, 39, 2245.

or collodion, which would not prevent the passage of ions but would avoid mixing of the solutions, has been suggested; * such membranes, however, probably introduce additional potentials.† The same objection has been raised against the use of gels containing dissolved salts to act as intermediate between two solutions.‡ Making the liquid junction in a capillary tube delays mixing but introduces other errors; § in an interesting modification of this device the junction is actually made in a wide tube but almost immediately the connecting tube narrows to a capillary and diffusion is prevented.¶ The same principle is involved in the formation of the liquid junction in the space between a ground-glass plug and its seating.** For approximate work membranes, gels or capillary junctions are often used; alternatively, diffusion may be hindered by plugging the ends of the connecting tubes with cotton-wool, or tightly rolled filter paper.††

An advance in the setting up of reproducible liquid junctions was made by Lamb and Larson ‡‡ who devised the 'flowing junction'. The original junction of this type, and the earlier modifications §§ were made by allowing an upward current of the heavier electrolyte to meet a downward flow of the less dense solution, at a point where a horizontal tube joins the main tube (Fig. 22, A). The levels of the liquids are so arranged that they flow at the same slow speed, and a sharp boundary is maintained. A very simple and effective type of flowing junction has been used by Roberts and Fenwick; ||| a thin mica plate is interposed vertically between the ends of two horizontal tubes along which the separate electrolytes stream slowly. The solutions flow down opposite faces of the plate past a small hole, through which alone the solutions make contact (Fig. 22, B). It has been claimed that reproducible flowing junctions can be set up by allowing jets of the two liquids to impinge

* See Fales and Stammelmann, *ibid.*, 1923, 45, 1271.

† Prideaux, *Trans. Faraday Soc.*, 1914, 10, 610; 1924, 20, 37; cf. also Ort and France, *J. Physical Chem.*, 1929, 33, 801; Oka, *J. Soc. Chem. Ind. Japan*, 1933, 36, 65, 66, 93.

‡ Lamb and Larson, *J. Amer. Chem. Soc.*, 1920, 42, 229.

§ Cumming and Gilchrist, *Trans. Faraday Soc.*, 1913, 9, 174.

¶ Clark (W. M.) and Cohen (B.), *U.S.A. Hygienic Lab. Bull.*, No. 151, 1928, p. 31.

** Hammett and Dietz, *J. Amer. Chem. Soc.*, 1930, 52, 4795; Ashton and Partington, *Trans. Faraday Soc.*, 1934, 30, 598.

†† Müller (E.), *Die Elektrometrische Massanalyse*, 1923, p. 11; for other methods of establishing liquid junctions, see Walpole, *loc. cit.*; Lewis, Brighton and Sebastian, *loc. cit.*; Ingham and Morrison, *J. Chem. Soc.* 1933, 1200.

‡‡ *Loc. cit.*

§§ MacInnes and Yeh, *J. Amer. Chem. Soc.*, 1921, 43, 2563; Scatchard, *ibid.*, 1925, 47, 696.

||| *Ibid.*, 1927, 49, 2787.

on one another; the apparatus is similar to that shown in Fig. 22, B, but the mica plate is unnecessary.* The actual potential at a flowing junction is probably different from that at a stationary junction, but the former is remarkably constant and reproducible. According to Roberts and Fenwick the measured potential of their flowing junction agreed with the value calculated by the Lewis and Sargent formula.†

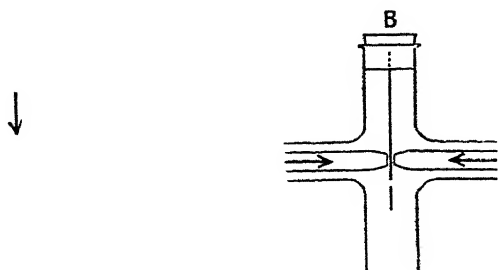


FIG. 22.—Flowing junctions

Single Electrode Potentials—The potential between a metal and a solution, making up a 'half-element', can only be determined by measuring the *E.M.F.* of a cell produced by combining this with another standard half-element of *known* potential difference; since the *E.M.F.* of the cell is the algebraic difference of the two separate potentials that of the unknown half-element may be evaluated. An important standard electrode consists of mercury in contact with a solution of potassium chloride saturated with mercurous chloride; this is known as the 'calomel electrode', the title being preceded by the concentration of the potassium chloride solution. The latter is generally 1.0*N* or 0.1*N*, but sometimes a saturated solution is used (for further details, see p. 327). Various attempts have been made to determine the *absolute* difference in potential between the mercury and the chloride solution in the calomel electrode; these methods depend on the establishment of a 'null electrode', i.e. a half-cell in which there is no difference of potential between metal and solution. The *E.M.F.* of a cell made by combining a null electrode with a calomel electrode gives directly the absolute potential of the latter.

* Lakhani, *J. Chem. Soc.*, 1932, 179; see also, Ghosh (D. N.), *J. Indian Chem. Soc.*, 1935, 12, 15.

† For theoretical and practical considerations of various types of liquid junction, see MacLagan, *Biochem. J.*, 1929, 23, 309; Unmack and Guggenheim, *Kgl. Danske Videnskabs. Selsk. Math.-fys. Medd.*, 1930, 10, [8]; Guggenheim, *J. Amer. Chem. Soc.*, 1930, 52, 1315; Scatchard and Buehrer, *ibid.*, 1931, 53, 574; Ferguson, *et al.*, 1932, 54, 1279, 1285.

Determination of Absolute Potential of the Calomel Electrode.*—Electrocapillary Method—If mercury is placed in contact with a liquid, e.g. dilute hydrochloric acid, the former becomes positively and the latter negatively charged; this difference of potential tends to increase the area of the surface of contact, and hence to decrease the interfacial tension. Any decrease in the double-layer potential results in an increase of the tension; when the mercury and the liquid are at the same potential the interfacial tension is a maximum. If an *E.M.F.* is applied from an external battery so as to make the mercury more negative and the solution positive, the interfacial tension is a maximum when the applied potential exactly balances the initial potential difference between the mercury and the solution. The interfacial tension is determined by finding the pressure which has to be applied to the mercury so as to bring the mercury-liquid interface back to a definite level in a capillary tube; the pressure is a maximum when the interfacial tension is a maximum. The *E.M.F.* is applied between the mercury forming the interface and a layer of mercury at the bottom of the vessel containing the solution; at the point of maximum interfacial tension the potential at the mercury in the capillary is zero; hence the applied *E.M.F.* is equal to the *absolute* potential at the bottom mercury layer. If the solution is *N*-potassium chloride the value is that of the 'normal' calomel electrode; working in this way Rothmund† determined the latter as + 0.56 volt. In a method depending on the same principle, but involving a different experimental technique, Bennewitz‡ has found the absolute potential of the *N*-calomel electrode to be - 0.19 volt!

The Drop Electrode—If a fine stream of mercury drops is allowed to flow into a mercurous salt solution positive ions will deposit on the fresh mercury surface, possibly on account of its low solution pressure, and be carried down with the drops; an equivalent quantity of anions will be carried down by electrostatic attraction. At the bottom of the vessel the mercury drops run together, and the reduction in surface area results in the liberation of the attracted ions which now enter the electrolyte. In this way mercurous salt is carried from the upper to the lower part of the solution; this process continues until the upper solution is so depleted of mercurous ions that there is no potential difference between the mercury drops and the solution, i.e. the solution pressure and osmotic pressure are equal. The drop electrode then constitutes

* For review and bibliography to 1907, see Palmaer, *Z. physikal. Chem.*, 1907, 59, 129.

† *Z. physikal. Chem.*, 1894, 15, 1; see also van Laar, *ibid.*, 1902, 41, 385.

‡ *Ibid.*, 1927, 125, 144.

a 'null electrode'. If the solution happens to be *N*-potassium chloride saturated with calomel, the *E.M.F.* of the cell formed by the drop electrode, when it has reached its null condition, and the mercury layer at the bottom of the vessel is equal to the absolute potential of the latter, i.e. of the 'normal' calomel electrode.* The value found in this way was + 0.56 volt, in agreement with Rothmund's result.

A modified drop electrode method was suggested by Nernst; a solution is prepared in which both dropping and stationary electrodes have the same potential. In such a solution both must be null electrodes, and by combining the stationary electrode with a calomel electrode the potential of the latter may be determined. Palmaer† succeeded in preparing a 'null solution' containing 0.1 gm. equiv. potassium chloride, 0.01 gm. equiv. potassium cyanide, 0.0008 gm. equiv. potassium hydroxide and 0.00025 gm. mol. of mercuric cyanide per litre; against this solution the potential of a normal calomel electrode was + 0.52 volt.

Movement of Fine Particles ‡—Fine particles of metal move in a solution under the influence of a fall of potential; but if the concentration is so altered that the particles no longer move, Billitzer assumed there was no difference of potential between metal and solution. Colloidal particles of mercury, lead and silver, as well as minute balls of metal suspended on quartz fibres, were used; in other experiments fine metal powders were allowed to fall through the electrolyte. In every case a null solution was prepared in which the applied *E.M.F.* had no influence on the metal particles; the assumption was then made that the *massive* metal placed in the same solution would also constitute a null electrode. By combining this with a normal calomel electrode the potential of the latter was found to be roughly - 0.18 volt; a value very different from those obtained previously. Billitzer's experiments have been repeated§ but the results could not be confirmed.

Christiansen's Method ||—It has been observed** that if a mercury drop falls vertically into a solution through which an elec-

* Ostwald, *ibid.*, 1887, 1, 583; Paschen, *Ann. Physik*, 1891, 43, 585; Palmaer, *Z. physikal. Chem.*, 1898, 25, 265; 1899, 28, 257; 1901, 39, 664; Krüger and Krummreich, *Z. Elektrochem.*, 1913, 19, 617, 622.

† *Ibid.*, 1903, 9, 754.

‡ Billitzer, *ibid.*, 1902, 8, 638; see also *Z. physikal. Chem.*, 1904, 48, 513; 1905, 51, 166. For reviews, see *Monatsh.*, 1929, 53-4, 813; *Trans. Amer. Electrochem. Soc.*, 1930, 57, 351; *Z. Elektrochem.*, 1931, 37, 736.

§ Whitney and Blake, *J. Amer. Chem. Soc.*, 1904, 26, 1339; Goodwin and Sosman, *Trans. Amer. Electrochem. Soc.*, 1905, 7, 83.

|| See Freundlich, *Colloid and Capillary Chemistry*, 1926, Eng. trans., p. 302.

** Christiansen, *Ann. Physik*, 1903, 12, 1072.

tric current is passing, the drop is deflected to the right or left according to the potential difference between it and the solution. When there is no deflection there is presumed to be no difference of potential between the mercury and the electrolyte; in this way a null electrode may be obtained. Frumkin* prepared a null solution by adding mercuric chloride and potassium cyanide to a potassium chloride solution; the normal calomel electrode was thus found to have a potential of about $+0.53$ volt.

Bodforss† used a similar principle, but the mercury drop was placed in a horizontal tube and the mercurous ion concentration of the solution altered until the drop did not move under the influence of a fall of potential. The standard calomel electrode gave an absolute potential of $+0.40$ volt by this method.

Garrison's Method ‡—A cylindrical glass trough was closed at the bottom with a circular silver plate divided by vertical glass partitions into four quadrants insulated from one another; opposite pairs of segments were connected together and charged by the opposite poles of a battery. A solution of a silver salt was placed in the trough, and the current flowed up from one pair of quadrants, over the glass partitions and down to the other pair. A flat silver needle was suspended horizontally in the solution just over the glass partitions; if the needle were positively charged with respect to the solution it should rotate in the direction of the current, but if negatively charged it should move in the opposite direction. The silver ion concentration of the solution was altered until the silver needle showed no movement; there was then supposed to be no difference of potential between metal and solution. By connecting this null electrode with a normal calomel electrode the potential of the latter was found to be between -0.10 and -0.20 volt.

Method of Bennewitz and Schulz §—Two similar silver electrodes are placed in a solution of a silver salt and connected through a galvanometer; one of the electrodes is rubbed so as to disturb the double-layer and current flows through the galvanometer to restore the equilibrium. The solution is diluted and ammonia is added until rubbing causes no flow of current; there is then no double-layer and either electrode may be regarded as a null electrode. The normal calomel electrode potential was determined in this manner as -0.19 volt.

* *J. Russ. Phys. Chem. Soc.*, 1917, 49, I, 207; *Chem. Abs.*, 1923, 17, 3276.

† *Z. Elektrochem.*, 1923, 29, 121.

‡ *J. Amer. Chem. Soc.*, 1923, 45, 37.

§ *Z. physikal. Chem.*, 1926, 124, 115; see also, Bennewitz and Bigalki, *ibid.*, 1931, 154, 113.

Andauer's Method * introduces an entirely new principle; a metal gauze connected to earth was placed above and parallel to the surface of a solution, and surmounted by a parallel plate connected to an electrometer. Air in the neighbourhood of the gauze was ionized by a constant radioactive source, and the potential between the metal plate and a standard electrode, e.g. calomel, immersed in the solution was determined by measurements of the leakage current from the charged electrometer. The potential at the metal-air and air-solution interfaces were neglected, and the absolute potential of the N-calomel electrode was found to be $+0.51$ volt. Subsequently † it was found that the metal-air potential could not be neglected, and making allowance for this altered the absolute value of the calomel electrode to about -0.2 volt! In view of the uncertainty of the method and the neglect of the air-liquid potential the results do not yet merit serious consideration.

Review of Absolute Potentials—In examining the methods described for obtaining an electrode of zero potential it is seen that they all (except that of Andauer) depend on the annulment of the potential difference between a metal and a solution relative to which the metal *moves or tends to move*. If a relative displacement of electrolyte and metal occurred at the exact surface of separation between the two phases, then the null potential would be the true thermodynamic (or Nernst) potential between the metal and solution. Owing to the unsaturated condition of all surfaces, however, it is very probable that some ions and molecules present in the electrolyte will attach themselves to the metal by adsorptive or similar forces; the displacement of the two phases will occur between the film adhering to the metal and the main bulk of solution. The difference of potential between these layers which move relative to one another in an electrical field is called the 'electrokinetic potential', and in all the experiments described it is probably this potential which is annulled. The electrokinetic and thermodynamic potentials are not necessarily related; the former is known to be very markedly affected by surface active substances which hardly affect the latter. It is possible that in a limited number of cases the two potentials may be connected,‡ but in recent years there has been a growing consensus of opinion favouring the view that this connection is the exception rather than the rule.§ In view of this fundamental objection many other weak-

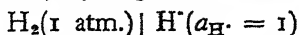
* *Z. physikal. Chem.*, 1927, 125, 135. † *Ibid.*, 1928, 138, 357.

‡ See Krüger and Krummreich, *loc. cit.*; Baur, *Trans. Faraday Soc.*, 1924, 19, 718.

§ Freundlich and Mäkel, *Z. Elektrochem.*, 1909, 15, 161; Gouy, *Ann. Chim. Phys.*, 1917, 7, 129; Frumkin, *Phil. Mag.*, 1920, 6, 363, 375; Gyemant, *Z. physikal. Chem.*, 1922, 103, 268; McBain, *J. Physical Chem.*, 1924, 28, 706; Usher, *ibid.*, 1926, 30, 954; Freundlich, *Trans. Faraday*

nesses which have been pointed out from time to time concerning the methods for the determination of the so-called 'absolute potential' need not be considered here.* It is clear that there must at present be some uncertainty concerning the absolute potential of any electrode, and pending the time when unequivocal results are available it is much more satisfactory to adopt an arbitrary standard for expressing differences of potential.

Potential Standard—Nernst† suggested that the potential difference between a hydrogen electrode with gas at 1 atmosphere (760 mm. of mercury) pressure and a solution containing hydrogen ions at a concentration of 1 gm. ion per litre be considered arbitrarily as zero at all temperatures.‡ Originally hydrogen ion concentrations were determined from conductance measurements, but as it is generally accepted that the conductance ratio does not give a true measure of the ionization of a strong electrolyte, the Nernst standard has been modified by the introduction of activities.§ In the definition of the arbitrary zero the *activity* of the hydrogen ion is supposed to be unity, and the resulting electrode is called the normal (or standard) hydrogen electrode; thus



is zero at all temperatures. Electrode potentials measured against this standard are called 'potentials on the hydrogen scale'; this scale will be adopted throughout the book. Although hydrogen electrodes are very reproducible they are not easily set up; hence a secondary standard electrode, viz. the calomel electrode, is generally used for reference purposes. It is, therefore, necessary to know the potential of various types of calomel electrode against the normal hydrogen electrode. Unfortunately there is no certainty in these matters,|| because (i) the calculation of *E.M.F.*'s against the hydrogen electrode of unit ionic activity involves extrapolation of

Soc., 1926, 22, 440; Coehn and Schafmeister, *Z. physikal. Chem.*, 1927, 125, 401; Procopiu, *ibid.*, 1931, 154, 322.

* Smith (S. W. J.), *Phil. Trans.*, 1900, 193 A, 47; *Phil. Mag.*, 1908, 15, 478; Lewis (W. C. McC.), *Z. physikal. Chem.*, 1910, 73, 146; Heyrovsky, *Proc. Roy. Soc.*, 1923, 120 A, 628; Liebreich, *Z. Elektrochem.*, 1926, 32, 162; see, however, Baur, *ibid.*, 1932, 38, 665.

† *Ibid.*, 1900, 5, 253. Since the hydrogen electrode in practice involves the use of a metal, the measured potential will include the Volta potential (see p. 359) which will vary with the nature of the metal; for this reason the hydrogen electrode is theoretically an unsatisfactory standard (see *Trans. Faraday Soc.*, 1931, 27, 239).

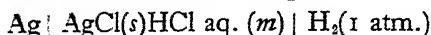
‡ See Auerbach, *Z. Elektrochem.*, 1912, 18, 13.

§ Lewis, *J. Amer. Chem. Soc.*, 1913, 35, 1; Lewis and Randall, *Thermodynamics*, 1923, p. 405.

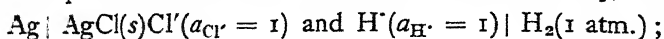
|| See Scatchard, *J. Amer. Chem. Soc.*, 1925, 47, 696; Cohn *et al.*, *ibid.*, 1928, 50, 696; Randall and Young (L. E.), *ibid.*, p. 989; Clark, *The Determination of Hydrogen Ions*, 1928, Chap. XXIII.

measurements made in very dilute solutions (see p. 363); (ii) individual ion activities cannot be known exactly; and (iii) liquid junction potentials cannot be completely eliminated, nor can their values be determined with any certainty.

The following method may be used to determine the potentials of the various calomel electrodes on the hydrogen scale. From measurements made on cells of the type



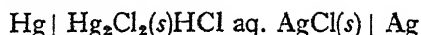
it has been found that when the acid is at unit activity, the *E.M.F.* (E_0) is $+0.2222$ volt at 25° .^{*} The cell may then be considered as made up of two electrodes with ions at unit activity, thus



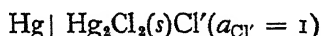
since the mean activity of hydrochloric acid is equal to $\sqrt{a_{\text{H}'} \times a_{\text{Cl}'}}$, it is also unity. The potential of the right-hand electrode is by definition zero; hence

$$\text{Ag} | \text{AgCl}(s) | \text{Cl}'(a_{\text{Cl}'} = 1) = 0.2222 \text{ volt.}$$

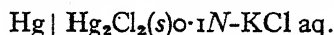
The *E.M.F.* of the cell



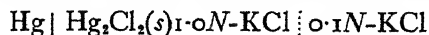
is 0.0455 volt,[†] independent of the acid strength, and so the potential of



must be $0.2222 + 0.0455 = 0.2677$. The activity coefficient of the chlorine ion in $0.1N$ -potassium chloride is taken as 0.7704 ,[‡] and the activity is then 0.07704 ; the potential of the half-element



is thus $0.2677 - 0.0591 \log 0.07704$, i.e. 0.3335 volt. This is the potential of the 'tenth-normal' calomel electrode at 25° , on the hydrogen scale; § it is quite free from any liquid junction potentials. The *E.M.F.* of a cell consisting of 'deci-normal' and 'normal' calomel electrodes, including liquid junction potential, is 0.0529 volt; hence the potential of the electrode



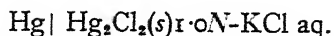
^{*} For details of the method, *vide infra* p. 363.

[†] Gerke, *J. Amer. Chem. Soc.*, 1922, **44**, 1684; Randall and Young, *loc. cit.*

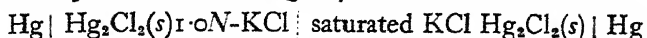
[‡] See Spencer (H. M.), *ibid.*, 1932, **54**, 3647, 4490. A disadvantage of the hydrogen electrode standard is evident here from the fact that it is necessary to assume that the activity of the chlorine ion in potassium chloride solution is the same as the mean ionic activity.

§ The value given in International Critical Tables, Vol. VI, p. 232, is 0.3334 ; Guggenheim and Schindler (*J. Physical Chem.*, 1934, **38**, 536) prefer 0.3337 volt.

is 0.2806 volt. The liquid junction potential is 0.0004 volt,* the more dilute solution being positive; the potential of the normal calomel electrode



is thus 0.2810 volt at 25°. The calomel electrode with saturated potassium chloride has the advantage of the elimination of at least one liquid junction potential when the same solution, as is often the case, is used as intermediate liquid. Its temperature coefficient (*vide infra*) is, however, higher than those of the other calomel half-elements. The electrode was devised by Michaelis and has been examined by Fales and Mudge;† the *E.M.F.* of the cell



is 0.0388, and as the liquid junction potential is 0.0002, the potential difference of the 'saturated' calomel electrode is 0.2420 volt at 25°.

Temperature Coefficients—There is some confusion in the literature concerning the values of temperature coefficients; the fundamental standard that the normal hydrogen electrode has a potential of zero at all temperatures is not always adhered to.‡ From the results given by Clark§ the following temperature coefficients may be calculated as applicable between about 15° and 40°:

0.1N-KCl	Calomel	.	.	— 0.00007 volt/degree
1.0N-KCl	"	.	.	— 0.00024 " "
Saturated KCl	"	.	.	— 0.00076 " "

Thus the potential of the 'normal' calomel electrode is given by the expression $0.2810 - 0.00024(t^\circ - 25)$ volt.

Preparation of Calomel Electrodes—In order to obtain reproducible half-elements it is essential that the mercury and mercurous chloride should be quite pure; the latter must be free from mercuric compounds and not too finely divided.¶ For general laboratory work a simple electrode vessel (Fig. 23) or a 2- or 4-oz. wide-mouthed bottle may be used; a small quantity of pure mercury is placed at the bottom of the vessel and covered with a paste of pure mercurous chloride, mercury and potassium chloride solu-

* Fales and Vosburgh, *J. Amer. Chem. Soc.*, 1918, 40, 1291.

† *Ibid.*, 1920, 42, 2434; see also Ewing, *ibid.*, 1925, 47, 301; Riehm, *Z. physikal. Chem.*, 1932, 160, 1.

‡ See Bircher and Howell, *J. Amer. Chem. Soc.*, 1926, 48, 34.

§ *Op. cit.*, Chap. XII.

¶ Richards, *Z. physikal. Chem.*, 1897, 24, 39; Sauer, *ibid.*, 1904, 47, 146; Lewis and Sargent, *J. Amer. Chem. Soc.*, 1909, 31, 362; for methods of preparing pure mercury and mercurous chloride, see Hulett, *Phys. Rev.*, 1911, 33, 307; Lipscomb and Hulett, *J. Amer. Chem. Soc.*, 1916, 38, 22; Ewing, *loc. cit.* Even traces of bromide must be avoided in the calomel, see Hahn, *ibid.*, 1935, 57, 2537.

tion. The electrode vessel is then filled with the appropriate solution of potassium chloride which has previously been saturated with calomel. Electrical connection with the mercury is made by

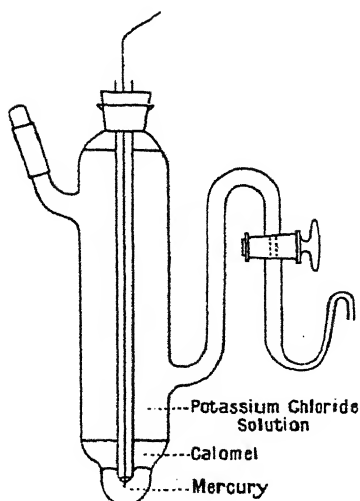


FIG. 23.—Standard calomel electrode vessel

a piece of platinum wire, sealed into a glass tube, dipping into the mercury at the bottom of the vessel; a suitable syphon tube filled with potassium chloride solution allows connection to be made with another electrode. Various types of vessels have been used for calomel electrodes; * the object of the special design is generally to prevent diffusion of the second electrolyte into the potassium chloride solution.

Other Standard Electrodes

—Although the calomel electrode is almost invariably used as it is a very reliable standard, for some purposes it is convenient, e.g. to avoid introducing another electro-

lyte, to have standards containing alkali or acid. Such are, for example, the $\text{Hg}|\text{HgO}$ alkali electrode,† and the $\text{Hg}|\text{Hg}_2\text{SO}_4$ sulphuric acid half-element.‡ Another type of standard half-element which is readily set up and easily reproducible consists of a clean platinum wire or foil inserted in a solution of 0.01N-HCl and 0.09N-KCl saturated with quinhydrone (cf. p. 378); the potential of this electrode is + 0.5826 volt at 18° on the hydrogen scale.§

Evaluation of Single Potentials on the Hydrogen Scale

—In order to measure the potential of a single electrode the latter is set up in some suitable vessel, and combined with a standard electrode in order to form a complete cell. The electrolytes in

* See Clark, *op. cit.*, p. 304; Parker and Dannerth, *Ind. Eng. Chem.*, 1925, 17, 637 (for industrial purposes).

† Donnan and Allmand, *J. Chem. Soc.*, 1911, 99, 845; see also Knobel, *J. Amer. Chem. Soc.*, 1923, 45, 70; Samuelson and Brown (D. J.), *ibid.*, 1935, 57, 2711.

‡ See Wilsmore, *Z. physikal. Chem.*, 1900, 35, 296; Wolff and Waters, *Bull. Bureau Stand.*, 1907, 3, 625; Bircher and Howell, *loc. cit.*; Glover, *J. Chem. Soc.*, 1933, 10.

§ Veibel, *ibid.*, 1923, 123, 2203; Hovorka and Dearing (*J. Amer. Chem. Soc.*, 1934, 56, 243) consider it to be more reliable than the calomel electrode as a standard.

the two half-elements are connected by dipping the syphon tubes of the electrode vessels into a vessel containing either of the two solutions, or better by means of a flowing junction. If an attempt to eliminate the junction potential is to be made, ammonium nitrate or potassium chloride solution may be placed in the intermediate vessel. The *E.M.F.* of the cell is then measured; if the value is E , and the calomel electrode (π_c) is the positive electrode of the cell, the potential of the other (π_x) is given by

$$\pi_c - \pi_x = E. \quad \therefore \pi_x = \pi_c - E.$$

If the calomel is the more negative electrode,

$$\pi_x - \pi_c = E, \text{ and } \pi_x = E + \pi_c.$$

Thus the *E.M.F.* of the cell



is 1.084 volt, and the calomel is positive; hence the potential of the zinc electrode is $0.281 - 1.084 = -0.803$ volt. On the other hand in the cell



the calomel is negative, and the numerical *E.M.F.* of the cell is 0.017 volt; therefore the potential of the copper electrode is $0.017 + 0.281 = +0.298$ volt. If liquid junction potentials are included they must be allowed for.

Standard or Normal Electrode Potentials—It has been shown that on the basis of the Nernst theory, modified by the activity concept, the single potential of a metal may be expressed by the formula

$$\pi = \pi_0 + \frac{RT}{nF} \ln a_+ \quad (\text{xx})$$

or of a non-metal (yielding negative ions) by

$$\pi = \pi_0 - \frac{RT}{nF} \ln a_- \quad (\text{xxiii})$$

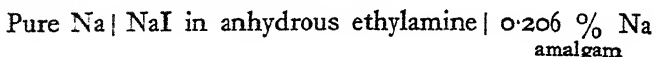
In either case when the ions are at unit activity the potential is equal to the constant π_0 ; this value is called the standard, or normal, electrode potential of the metal or non-metal. By definition the standard potential of the hydrogen electrode is zero at all temperatures.* The earliest tabulation of normal electrode potentials was made by Wilmore† and revised by Abegg, Luther and Auer-

* Where the activity concept has not been adopted the 'normal potential' is defined as the value in a solution containing 1 gm. ion of the reversible ion per litre; the ionic concentration is determined from the conductance ratio and the treatment is approximate.

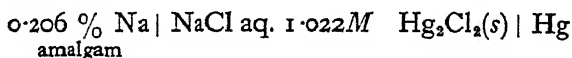
† *Z. physikal. Chem.*, 1900, 35, 291.

bach; * subsequently Lewis and Randall † re-calculated standard potentials using activity data. If the activity of the reversible ion is known and the electrode potential (π) determined in that solution, the standard electrode potential (π_0) could be calculated by equations (xx) or (xxiii). Since individual ion activities cannot be determined, and as the measurement of the potential of a single electrode often involves the inclusion of the potential of a liquid junction, special procedures have to be adopted in practice.

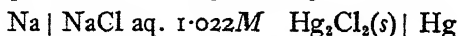
As an example of the methods used to determine standard electrode potentials the interesting case of sodium will be described, as an illustration of the procedure adopted for a metal which attacks water. The *E.M.F.* of the cell



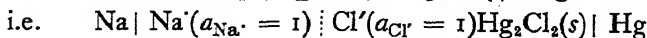
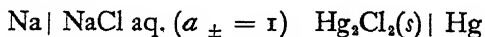
is constant and reproducible and independent of the concentration of the sodium iodide solution; its value is -0.8453 volt at 25° . ‡ The dilute amalgam is not attacked if left in contact with an aqueous solution for a short time, and by the use of a device which allowed the amalgam surface to be continually renewed the potential of the amalgam against a sodium chloride, or other, solution could be measured. Thus from the results of Allmand and Polack § the *E.M.F.* of the cell



has been interpolated as -2.1582 at 25° ; hence



is $-2.1582 + (-0.8453) = -3.0035$ volt. The activity coefficient of $1.022 M$ sodium chloride is taken as 0.650 , and so the *E.M.F.* of the cell



is $-3.0035 - 0.0591 \log(1.022 \times 0.650)$, i.e. -2.9825 volt. Since the value of the right-hand electrode is probably 0.2677 (*supra* p. 326), the standard electrode potential of sodium is calculated as 2.7148 at 25° . The more important standard electrode potentials for metals, mainly taken from the International Critical Tables, Vol. VI, 1929, pp. 332, 333, are given in Table XLV; || values for non-metals will be considered later.

* *Abh. Bunsen-Ges.*, 1911, No. 5. † *Thermodynamics*, 1923.

‡ Lewis and Kraus, *J. Amer. Chem. Soc.*, 1910, 32, 1459.

§ *J. Chem. Soc.*, 1919, 115, 1020.

|| For more recent measurements see: Potassium: Armbruster and Crenshaw, *J. Amer. Chem. Soc.*, 1934, 56, 2525; Calcium: Shibata,

TABLE XLV
STANDARD ELECTRODE POTENTIALS AT 25°.

Li, Li ⁺	- 2.959	Tl, Tl ⁺	- 0.33
Rb, Rb ⁺	- 2.926	Co, Co ⁺⁺	- 0.28
K, K ⁺	- 2.924	Ni, Ni ⁺⁺	- 0.23
Ca, Ca ⁺⁺	- 2.76	Sn, Sn ⁺⁺	- 0.136
Na, Na ⁺	- 2.715	Pb, Pb ⁺⁺	- 0.122
Mg, Mg ⁺⁺	- 1.55	H, H ⁺	= 0
Al, Al ⁺⁺⁺	- 1.33	Sb, Sb ⁺⁺⁺	+ 0.1
Mn, Mn ⁺⁺	- 1.1	Bi, Bi ⁺⁺⁺	+ 0.226
Zn, Zn ⁺⁺	- 0.762	Cu, Cu ⁺⁺	+ 0.344
Cr, Cr ⁺⁺	- 0.557	Ag, Ag ⁺	+ 0.799
Fe, Fe ⁺⁺	- 0.441	Hg, Hg ₂ ⁺⁺	+ 0.799
Cd, Cd ⁺⁺	- 0.401	Au, Au ⁺⁺⁺	+ 1.36

The accuracy of the standard potentials quoted above is frequently limited by a lack of knowledge of ionic activities: this is, however, not serious. The chief use of the standard potential is that it allows the potential of an electrode to be calculated if the activity of the ions is known: in actual practice the mean activity only is available, at best, and it is therefore possibly an advantage for the standard potential to be expressed in analogous, if not identical, terms. It is evident that the true standard potential is generally more of thermodynamic than of physical significance, for it can only be employed if individual ionic activities are known. In practice the approximation is made of assuming the latter to be equal to the mean value for the electrolyte, and sometimes the further approximation is used in which the electrode potential is represented by

$$\pi = \pi_0 + \frac{RT}{nF} \ln \alpha c$$

where α is the conductance ratio, and c the molar concentration of the salt yielding the reversible ion.

When metals are arranged in order of their standard electrode

J. Sci. Hiroshima Univ., 1931, [A], 1, 147; Beryllium: Prytz, *Z. anorg. Chem.*, 1930, 193, 113; Zinc: Getman, *J. Physical Chem.*, 1930, 35, 2749; Shrawder, Cowperthwaite and La Mer, *J. Amer. Chem. Soc.*, 1934, 56, 2348; Gallium: Bergkamp, *Z. Elektrochem.*, 1932, 38, 847; Iron: Randall and Frandsen, *J. Amer. Chem. Soc.*, 1930, 52, 589; Murata, *J. Soc. Chem. Ind. Japan*, 1932, 35, 209; Müller (E.) and Janitzki, *Z. physikal. chem.*, 1932, 160, 245; see, however, Bodforss, *ibid.*, p. 141; Cadmium: Getman, *J. Physical Chem.*, 1930, 35, 588; Shrawder *et al.*, *loc. cit.*; Cobalt: Heymann and Jellinek, *Z. physikal. Chem.*, 1932, 160, 34; Haring and Westfall, *Trans. Amer. Electrochem. Soc.*, 1934, 65, 61; Nickel: Colombier, *Compt. rend.*, 1934, 199, 273; Lead: Randall and Cann, *J. Amer. Chem. Soc.*, 1930, 54, 589; Cann and La Rue, *ibid.*, 1932, 54, 3456; Bismuth: Haissinsky, *Compt. rend.*, 1934, 199, 1397; Silver: Chloupek and Daneš, *Coll. Czech. Chem. Comm.*, 1932, 4, 165.

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potentials there is obtained the so-called 'electromotive series, of the elements; in general the metals with the more negative potentials, i.e. base metals, will displace those with more positive potentials from their solutions. This subject will be discussed more fully subsequently.*

* Although potentials on the hydrogen scale are adopted throughout this book the convention is not universal; sometimes the 'normal' calomel electrode is adopted as zero, and sometimes potentials are expressed on the so-called 'absolute' scale, i.e. *N*-calomel = + 0.560 volt. If *h* is the potential of a given electrode on the hydrogen scale, *c* on the calomel scale, and *a* on the absolute scale, then

$$c = h - 0.281 \text{ at } 25^\circ$$

$$\text{and} \quad a = c + 0.560$$

$$= h + 0.279 \text{ at } 25^\circ.$$

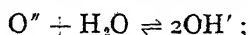
CHAPTER XIV

REVERSIBLE CELLS—III

GAS Electrodes and Gas Cells.—The Oxygen Electrode—If oxygen gas is circulated round a platinized platinum electrode dipping into an aqueous solution, as for a hydrogen electrode, a more or less definite potential is attained which depends on the pressure of the gas and the nature of the electrolyte. The oxygen dissolved in the platinum may be regarded as being in equilibrium with *negative* oxygen ions (O'') in the solution; applying the solution pressure theory it may be shown that

$$\pi = \text{constant (i)} - \frac{RT}{2F} \ln a_{O''} \quad (\text{i})$$

The oxygen ions are probably in equilibrium with OH' ions, thus



hence

$$a_{OH'}^2/a_{O''} = \text{a constant},$$

if the activity of the water is assumed to be constant. It follows then that

$$\pi = \text{constant (ii)} - \frac{RT}{F} \ln a_{OH'} \quad . \quad . \quad . \quad (\text{ii})$$

Further, since $a_{H^+} \times a_{OH'}$ is equal to K_w , the ionic product of water, it is seen that

$$\pi = \text{constant (iii)} + \frac{RT}{F} \ln a_{H^+} \quad (\text{iii})$$

The potential of an oxygen electrode therefore depends on the hydroxyl ion, and on the hydrogen ion, activity of the electrolyte. The values of the constants (i), (ii) and (iii) depend on the pressure of the gas.

If two oxygen electrodes at different pressures, p_1 and p_2 , are immersed in the same electrolyte, and the *E.M.F.* of the resulting cell is E , the electrical work involved in the transfer of 1 gm. mol. of gas from p_1 to p_2 is $4EF$; * the corresponding free energy change

* $O_2 \rightarrow 2O$; $+ 4e^- \rightarrow 2O''$, i.e. 4 faradays are involved.

is $RT \ln p_1/p_2$, if the gas laws are obeyed, and so

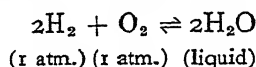
$$E = \frac{RT}{4F} \ln \frac{p_1}{p_2} \quad (\text{iv})$$

This equation does not include any convention as to the sign of the *E.M.F.*; since oxygen yields negative ions its sign as written in equation (iv) should be opposite in direction to that of the hydrogen cell the *E.M.F.* of which is represented by equation (xliii) on p. 310.

Hydrogen-Oxygen Cell—The *E.M.F.* of a cell consisting of an oxygen and a hydrogen electrode in the same aqueous electrolyte is equal to $\pi_{\text{O}_2} - \pi_{\text{H}_2}$, where

$$\pi_{\text{O}_2} = \text{constant} + \frac{RT}{F} \ln a_{\text{H}^+}, \quad \text{and} \quad \pi_{\text{H}_2} = \text{constant} + \frac{RT}{F} \ln a_{\text{H}^+};$$

hence the required *E.M.F.* is a constant, dependent only on the pressures of the two gases, but *independent* of the hydrogen ion activity of the electrolyte. Since gas electrodes are generally at atmospheric pressure, the *E.M.F.* of the oxygen-hydrogen cell is usually stated for this pressure; the value may then be calculated as follows. The reaction occurring in the cell is



for the passage of 4 faradays; the free energy change of the process, by the van 't Hoff isotherm, is

$$-\Delta G = 4EF = RT \ln K - RT \ln \frac{p_{\text{H}_2\text{O}}^2}{p_{\text{H}_2}^2 \times p_{\text{O}_2}} \quad (\text{v})$$

where K is the equilibrium constant, and the p terms represent the arbitrary pressures existing in the cell. Since the partial pressure, i.e. vapour pressure, of the liquid water remains constant, and the pressures of oxygen and hydrogen gas are both unity, the equation reduces to

$$E = \frac{RT}{4F} \ln K' \quad (\text{vi})$$

where

$$K' = \frac{1}{p_{\text{H}_2}^2 \times p_{\text{O}_2}} \quad (\text{vii})$$

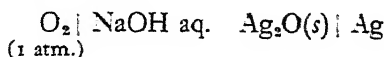
the p_e 's being the *equilibrium* pressures in *atmospheres*. The dissociation of water has been investigated at high temperatures,* and by means of the van 't Hoff isochore the equilibrium constant at 17° has been calculated; from this value the dissociation pressures

* Nernst and von Wartenberg, *Z. physikal. Chem.*, 1906, **56**, 534; cf. also Preuner, *ibid.*, 1902, **42**, 50.

of hydrogen and oxygen in equilibrium with liquid water have been determined. These are 3.438×10^{-29} and 1.719×10^{-29} atmospheres respectively, at 17° ; therefore for the oxygen-hydrogen cell at atmospheric pressure E may be calculated as 1.232 volt at 17° . Applying the Gibbs-Helmholtz equation (p. 287), the heat of reaction being taken as 136,800, the temperature coefficient of the cell is found to be -0.00085 volt degree; hence

$$E = 1.232 - 0.00085 (t^\circ - 17) \quad \dots \quad (\text{viii})$$

Lewis* used another method for calculating the *E.M.F.* of the oxygen-hydrogen cell; from the dissociation pressure of silver oxide the *E.M.F.* of the cell



was calculated (see p. 374) as 0.049 volt at 25° . Using Böttger's † value for the solubility product of silver oxide, the *E.M.F.* of the cell



was evaluated as 1.168 volt; hence the *E.M.F.* of the oxygen-hydrogen cell at 25° is 1.217 volt. Using a similar method to that of Lewis, but involving mercuric oxide, Brønsted ‡ determined the *E.M.F.* to be 1.234 volt at 17° . By means of the Nernst Heat Theorem it is possible to calculate the *E.M.F.* of the oxygen-hydrogen cell entirely from thermal data; the value so obtained is 1.225 at 17° .§ In view of the agreement between the various determinations of the *E.M.F.* of the oxygen-hydrogen cell the value may be taken as 1.22 at 25° ; this value is applicable in all aqueous electrolytes. In a solution of unit hydrogen ion activity the hydroxyl ion activity must be 10^{-14} ; by definition the hydrogen potential is zero, and so the oxygen potential must be 1.22 volt. Further since

$$\pi = \pi_0 - \frac{RT}{F} \ln a_{\text{OH}'} \quad (\text{ix})$$

it follows that the standard potential of oxygen at atmospheric pressure in a solution of hydroxyl ions of unit activity is +0.40 volt. From this value it is possible to calculate the potential of an oxygen electrode in any solution of known hydroxyl, or hydrogen ion, activity.

In actual practice the potential of an oxygen electrode is found to rise rapidly at first, then there is a drift lasting several days.

* *J. Amer. Chem. Soc.*, 1906, 28, 158; *Z. physikal. Chem.*, 1906, 55, 449; see also Britton, *J. Chem. Soc.*, 1925, 127, 2956.

† *Z. physikal. Chem.*, 1903, 46, 521.

‡ *Ibid.*, 1909, 65, 84, 744.

§ Nernst, *Sitzungsber. Berlin. Akad.*, 1909, 255; see Lewis, *A System of Physical Chemistry*, 1925, Vol. II, pp. 429-32.

The value reached is invariably lower than that expected from the calculated *E.M.F.* of the oxygen-hydrogen cell; the *E.M.F.* rises in a few hours to 1.08–1.09 volt, and then after several days to 1.14 volt.* The use of either iridium or smooth platinum as electrode metal does not bring the potential any nearer to the 'theoretical' value 1.22 volts. There is little doubt that the oxygen electrode, unlike the hydrogen electrode, is not truly reversible; in spite of this it has found some application in hydrogen ion measurements (p. 378). It is very probable that the electrode material, e.g. platinum or iridium, is oxidized when surrounded by oxygen, and it is the oxides which are responsible for the irreversibility of the electrodes.† If a polarized platinum anode (see Chap. XVI) is allowed to stand for some time in sulphuric acid its potential falls rapidly at first, and then remains constant at about 1.08 volt;‡ there is little doubt that such an electrode contains oxides of platinum, and the similarity of the potential to that of an ordinary oxygen electrode suggests that the latter also contains an oxide. It may be significant, too, that Grube found the potentials of platinum against $\text{PtO}_2 \cdot 2\text{H}_2\text{O}$ and PtO in 2*N.* sulphuric acid were 1.04 and about 0.90 volt respectively. The influence of pressure on the oxygen electrode is not at all in agreement with the requirements of the theoretical equation (iv); the results suggest the presence of an oxide on the electrode metal.§ Apparently, owing to the formation of these stable oxides the electrode never becomes saturated with oxygen gas.|| It is interesting to note that by using glass, porcelain or fused alkali as electrolyte, Haber** was able to measure the *E.M.F.* of the oxygen-hydrogen cell at temperatures from 330° to 1000° C.; under these conditions the oxides are unstable and the values obtained were very close to the calculated *E.M.F.*'s.

* Smale, *Z. anorg. Chem.*, 1894, **14**, 577; Crotochino, *ibid.*, 1900, **24**, 258; Bose, *Z. physikal. Chem.*, 1900, **34**, 730; Wilshire, *ibid.*, 1900, **35**, 291; Czepinski, *Z. anorg. Chem.*, 1902, **30**, 1; Westhaver, *Z. physikal. Chem.*, 1905, **51**, 83; Lorenz and Hauser, *Z. anorg. Chem.*, 1906, **51**, 81; Schoch, *J. Physical Chem.*, 1910, **14**, 665. For summary and references, see Hoar, *Proc. Roy. Soc.*, 1933, **142** A, 628.

† See Lorenz and Hauser, *loc. cit.*; Haber, *Z. anorg. Chem.*, 1906, **51**, 356. For a detailed mechanism, see Hoar, *loc. cit.*

‡ Foerster, *Z. physikal. Chem.*, 1909, **69**, 336; Lorenz and Spielmann, *Z. Elektrochem.*, 1909, **15**, 293, 349; Grube, *ibid.*, 1910, **16**, 621.

§ Tammann and Runge, *Z. anorg. Chem.*, 1926, **156**, 85.

|| The irreversibility of the oxygen gas electrode has also been attributed to the formation of hydrogen peroxide (Tartar and Wellman, *J. Physical Chem.*, 1928, **32**, 1171), or to the adsorption of ions (Tartar *et al.*, *J. Amer. Chem. Soc.*, 1930, **52**, 2256; 1931, **53**, 3201).

** *Z. anorg. Chem.*, 1906, **51**, 245, 289, 356; *Z. Elektrochem.*, 1906, **12**, 415.

Halogen Electrodes—A platinum electrode, coated with a thin film of platinum or iridium black, dipping in a solution of a halogen acid or salt, and surrounded by a halogen gives a definite potential; this depends on the activity of the free halogen and of the ions in the electrolyte. The former quantity may be stated in terms of pressure, e.g. for chlorine and bromine, or of solubility, as for iodine. In general the potential of a halogen electrode may be expressed as

$$\pi = \pi_0 - \frac{RT}{F} \ln a_{X'} \quad \dots \quad (x)$$

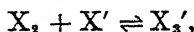
where $a_{X'}$ is the activity of the halogen ions, and π_0 is the standard potential in a solution of unit ion activity for a given electrode activity. The value of π_0 is generally given at a gas pressure of 1 atmosphere for chlorine, and for a saturated solution of iodine; with bromine it may be stated for the vapour at atmospheric pressure, for a saturated solution or for a molar solution. Although halogens behave quite reversibly the measurement of their potentials is attended with various difficulties. Firstly, chlorine is liable to attack the electrode, and the gas must be used at a low partial pressure; by applying the equation

$$E = \frac{RT}{2F} \ln \frac{p_1}{p_2}, \quad (xi)$$

deduced in exactly the same manner as for oxygen or hydrogen, the correction for atmospheric pressure may be determined. The sign of the *E.M.F.* is in the same direction as for the oxygen cell (see p. 334) since chlorine also yields negative ions. In the second place the reaction



occurs to a marked extent with chlorine and also with bromine; potentials are, therefore, measured in acid solution to avoid the disturbance resulting from this reaction. Thirdly, with bromine and iodine, perhalides are formed



and both free halogen and ions are removed in forming the perhalogen ion. Corrections for this source of error are determined from a knowledge of the equilibrium constant, $[X_3']/[X_2][X']$, of the reaction. The most recent values for the standard potentials are given in Table XLVI for 25°.*

* **Chlorine** : Lewis and Rupert, *J. Amer. Chem. Soc.*, 1911, 33, 299; Gerke, *ibid.*, 1922, 44, 1684; Randall and Young, *ibid.*, 1928, 50, 989; Kameyama, Yamamoto and Oka, *J. Soc. Chem. Ind. (Japan)*, 1926, 29, 679; **Bromine** : Lewis and Storch, *J. Amer. Chem. Soc.*, 1917, 39, 2544; Jones (G.) and Baeckström, *ibid.*, 1934, 56, 1524; **Iodine** : Jones (G.) and Kaplan, *ibid.*, 1928, 50, 2066.

TABLE XLVI

STANDARD POTENTIALS OF HALOGEN ELECTRODES AT 25°

Fluorine (1 atm.)	F' (a = 1)	2.85 volt.*
Chlorine (1 atm.)	Cl' (a = 1)	1.3583
Bromine (saturated)	Br' (a = 1)	1.066
Bromine (1 atm.)	Br' (a = 1)	1.085
Iodine (saturated)	I' (a = 1)	0.536

Although halogen electrodes could be applied for determining approximate halogen ion activities, the experimental difficulties and corrections necessary are so great as to preclude their general use; fortunately the activities may be determined by means of an electrode of the type $\text{Ag} | \text{AgX}(s) | \text{MX}$ solution, which is reversible with respect to the halogen X (see pp. 283, 302).

The *E.M.F.* of the cell



may be determined directly or it may be calculated, as in the case of the similar hydrogen-oxygen cell, from a knowledge of dissociation pressures. Alternatively these pressures may be calculated from the *E.M.F.*'s.

Gas electrodes involving sulphuretted hydrogen,† cyanogen,‡ ammonia, alone or mixed with hydrogen,§ ethylene,|| nitrogen,** carbon monoxide†† and acetylene‡‡ have been used in experimental work; these electrodes are mostly irreversible. §§

Oxidation-Reduction Cells—Oxidation involves a loss of electrons (gain of positive charge) and reduction a gain of electrons (loss of positive charge), and in a system containing both oxidized and reduced states there will be an equilibrium between them and electrons. When a metal is placed in a solution of its ions there is a tendency for the metal to lose electrons and form ions, whereas the ions tend to gain electrons and become atoms; here also there is an equilibrium between atoms, ions and electrons, and the position of the equilibrium is indicated by the electrode potential.

* Calculated by Latimer, *ibid.*, 1926, 48, 2868; see also, Simons and Hildebrand, *ibid.*, 1924, 42, 2223; Neumann and Richter, *Z. Elektrochem.*, 1925, 31, 481.

† Bernfeld, *Z. physikal. Chem.*, 1898, 25, 46.

‡ Naumann, *Z. Elektrochem.*, 1910, 16, 191.

§ Finkelstein *et al.*, *Acta Physicochim. U.R.S.S.*, 1935, 1, 805; Slade, *J. Chem. Soc.*, 1911, 99, 1974; 1914, 105, 1351.

|| Clarke, Myers and Acree, *J. Physical Chem.*, 1916, 20, 286.

** Usher and Venkateswaran, *J. Chem. Soc.*, 1919, 115, 613.

†† Hofmann and Wurthmann, *Ber.*, 1919, 52, 1185.

‡‡ Müller (R.) and Kumpfmüller, *Z. Elektrochem.*, 1928, 34, 70.

§§ See also, Krueger and Kahlenberg, *Trans. Amer. Elektrochem. Soc.*, 1930, 58, 341.

In exactly the same way an unattackable electrode, e.g. platinum, placed in an oxidation-reduction system will assume a definite potential indicative of the position of equilibrium; if the system is one which tends to bring about oxidation it will take up electrons from the platinum and leave it positively charged. On the other hand if the system has a reducing power it will give up electrons to the metal, which will then acquire a negative charge. The value of the electrode potential is thus an approximate measure of the oxidizing or reducing power of the system. Potential measurements of this type were made by Bancroft,* with a platinum electrode in 0.2 molar solutions of various oxidizing and reducing agents; some of the results, converted to the hydrogen scale, are given in Table XLVII. It will be seen later that these values are not really stable potentials, but they allow an interesting qualitative comparison of oxidizing and reducing power to be made; the former decreases down the series, and the latter increases.

TABLE XLVII

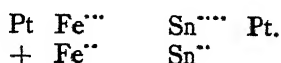
APPROXIMATE OXIDATION-REDUCTION POTENTIALS

Potassium permanganate	1.48 volt	Sodium sulphite	0.30 volt
Chromic acid . . .	1.12	Stannous chloride	
Ferric chloride . . .	0.96	(acid) . . .	0.22 "
Potassium dichromate	0.78	Hydroquinone . . .	-0.05 "
Potassium ferricyanide	0.70	Hydroxylamine . . .	-0.33 "
Sulphurous acid . . .	0.44	Alkali stannite . . .	-0.58 "
Ferrous sulphate . . .	0.35		

A *reversible* oxidation-reduction electrode may be obtained if the oxidized and reduced stages are both present, and each can be converted into the other by an infinitesimally small change of potential (cf. p. 283); † as examples may be taken the cases of ferric and ferrous ions, and stannic and stannous ions, viz.



Each of these systems gives a definite potential to a platinum electrode dependent on the *ratio* of the oxidized to reduced form. By combining two electrodes of this type an oxidation-reduction cell is obtained, thus :

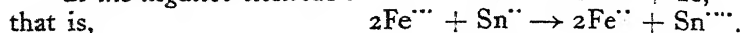
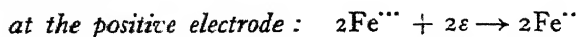


The ferric-ferrous electrode will, in general, be the more positive,

* *Z. physikal. Chem.*, 1892, 10, 837.

† On this basis many of Bancroft's electrodes were not reversible.

unless the concentration of ferric ions is very small; hence the reactions are:

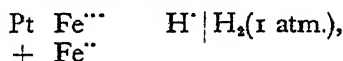


The cell may be regarded as a chemical cell in which the electrical energy is equivalent to the free energy change of the oxidation-reduction reaction, and in this case

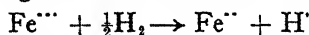
$$E = \frac{RT}{2F} \ln K - \frac{RT}{2F} \ln \frac{a_{\text{Sn}^{++++}} \times a_{\text{Fe}^{++}}^2}{a_{\text{Sn}^{++}} \times a_{\text{Fe}^{+++}}^2} \quad (\text{xii})$$

When the cell produces current there is a tendency for the potentials to become equalized; eventually the *E.M.F.* falls to zero when the activities have reached the equilibrium values. The *E.M.F.* of the cell, and also the separate potentials, thus depend on the relative concentrations (activities) of the oxidized and reduced forms.

Oxidation-Reduction Potentials *—The formula for the potential of an oxidation-reduction electrode may be determined thermodynamically. Consider the cell



that is, a platinum electrode dipping in a solution of ferric and ferrous salts, coupled with a hydrogen electrode; the latter will, in general, be the negative and hence the cell reaction is



for the passage of 1 faraday. Applying the van 't Hoff isotherm

$$-\Delta G = EF = RT \ln K - RT \ln \frac{a_{\text{Fe}^{++}} \times a_{\text{H}^+}}{a_{\text{Fe}^{+++}} \times a_{\text{H}}}, \quad (\text{xiii})$$

where K is the equilibrium constant of the reaction. It follows then that

$$E = \frac{RT}{F} \ln K - \frac{RT}{F} \ln \frac{a_{\text{Fe}^{++}}}{a_{\text{Fe}^{+++}}} - \frac{RT}{F} \ln \frac{a_{\text{H}^+}}{a_{\text{H}}}.$$

If the hydrogen gas is at one atmosphere pressure, and the activity of the ions is unity, the potential of the right-hand electrode is zero, and E is the value of the oxidation-reduction electrode potential on the hydrogen scale. In these circumstances a_{H^+} and a_{H} are both constants, and since R , T , F and K are constants, the terms

$$\frac{RT}{F} \ln K - \frac{RT}{F} \ln \frac{a_{\text{H}^+}}{a_{\text{H}}}$$

* Michaelis has suggested the use of the abbreviated term 'redox potentials', which is frequently found in biochemical literature.

may be put as equal to a constant π_0 . Substituting this value, and replacing E by π , which is the potential of the Pt $\left| \begin{smallmatrix} \text{Fe}^{+++} \\ \text{Fe}^{++} \end{smallmatrix} \right.$ electrode on the hydrogen scale,

$$\pi = \pi_0 + \frac{RT}{F} \ln \frac{a_{\text{Fe}^{+}}}{a_{\text{Fe}^{++}}} \quad \text{. (xiv)}$$

If the activities of the ferric and ferrous ions are equal, or the concentrations equal in dilute solution, $\pi = \pi_0$; the latter is called the normal or standard oxidation-reduction potential of the system. The actual potential π depends on the relative amounts of oxidized and reduced forms; in the presence of excess of the former a system will tend to have oxidizing powers, whereas an excess of the latter will lower the oxidation-reduction potential and the system will tend to bring about reducing reactions.

The accuracy of the equation for the oxidation-reduction potential, often called Peters' equation, was first tested with a series of mixtures of ferrous and ferric chlorides in 0.1N-hydrochloric acid; some of the actual measurements,* reduced to the hydrogen scale, are given in Table XLVIII. The activity coefficients of ferrous and ferric ions are assumed to be equal, that is $a_{\text{Fe}^{+++}}/a_{\text{Fe}^{++}}$ is taken as $[\text{Fe}^{+++}]/[\text{Fe}^{++}]$, and the values of π_0 are calculated.

TABLE XLVIII

OXIDATION-REDUCTION POTENTIALS OF FERRIC-FERROUS SYSTEM IN 0.1N-HYDROCHLORIC ACID AT 17°

Gm. Mols. per Litre		π	π_0	Mean
$[\text{Fe}^{+++}]$	$[\text{Fe}^{++}]$			
0.0005	0.0995	0.581	0.713	0.712
0.01	0.09	0.656	0.711	
0.03	0.07	0.691	0.712	
0.04	0.06	0.703	0.713	
0.05	0.05	0.714	0.714	
0.07	0.03	0.735	0.714	
0.09	0.01	0.763	0.708	

In view of the approximations involved and the uncertainty of liquid junction potentials the agreement with the theoretical requirements is good. Experiments with salts other than chlorides gave somewhat different results; these discrepancies may be due to (a) slowness with which the platinum electrode comes into true equilibrium with higher and lower ions,† and (b) the failure of the concentration ratios to represent the activity ratios. It has been stated that the equation

$$\pi = \pi_0 + \frac{RT}{F} \ln \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]}, \quad \text{. (xiva)}$$

* Peters, *Z. physikal. Chem.*, 1898, 26, 193.

† Luther, *Z. Elektrochem.*, 1907, 13, 289; in this paper the general criteria for stable electrode potentials are described.

which is applicable in dilute solutions, may be used for the analysis of solutions containing ferrous and ferric ions; it is claimed that the method is applicable at concentrations as low as 10^{-6} molar.*

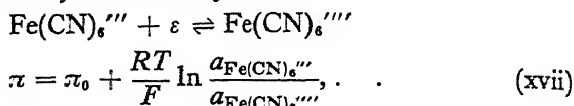
The general equation for the potential of an oxidation-reduction electrode involving the system



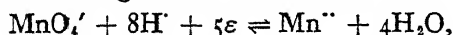
can be shown to be

$$\pi = \pi_0 + \frac{RT}{NF} \ln \frac{a_A^l \cdot a_B^m \cdot a_C^n \dots}{a_X^r \cdot a_Y^s \cdot a_Z^t \dots} \quad (\text{xvi})$$

where N is the number of electrons involved in the oxidation and reduction. This equation is applicable to a system consisting of anions only, viz. ferricyanide-ferrocyanide:



or to a system involving cations and anions, thus



when

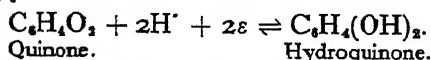
$$\pi = \pi_0 + \frac{RT}{5F} \ln \frac{a_{\text{MnO}_4'} \cdot a_{\text{H}^+}^8}{a_{\text{Mn}^{++}}} \quad (\text{xviii})$$

the activity of the water being considered constant. The potential of a peroxide electrode may also be regarded as due to an oxidation-reduction system between ions of higher and lower valency; the lead peroxide electrode has a potential dependent on the plumbic ion activity it is able to produce by dissolving in the electrolyte, and also on the plumbous ion activity, thus:

$$\pi = \pi_0 + \frac{RT}{2F} \ln \frac{a_{\text{Pb}^{++}}}{a_{\text{Pb}^{+}}} \quad (\text{xix})$$

Other oxide electrodes, e.g. MnO_2 , CuO , Ni_2O_3 , AgO , may be treated similarly (see also p. 375).

A number of organic oxidation-reduction systems have been found to be reversible and hence have been brought into line with inorganic reactions. Haber and Russ† showed that the reversible reduction of quinone to hydroquinone could be considered from the electrochemical standpoint; in acid solution the reaction may be regarded as:



The potential of an inert electrode, e.g. platinum, immersed in a

* Hirsch and Rüter, *Z. anal. Chem.*, 1926, 68, 328; Schischakov, *Analyst*, 1935, 60, 83.

† *Z. physikal. Chem.*, 1904, 47, 257.

solution containing quinone and hydroquinone should be given by

$$\pi = \pi_0 + \frac{RT}{2F} \ln \frac{a_Q a_H^2}{a_{H_2Q}} \quad \text{(xx)}$$

where a_Q and a_{H_2Q} are the activities of quinone and hydroquinone respectively; hence

$$\pi = \pi_0 + \frac{RT}{2F} \ln \frac{a_Q}{a_{H_2Q}} + \frac{RT}{F} \ln a_H \quad \text{(xxi)}$$

The oxidation-reduction potential of the quinone-hydroquinone system, as of most systems involving un-ionized organic compounds, is dependent on the hydrogen ion activity of the solution. This fact is utilized in a method for determining the latter (see p. 378). A large number of organic oxidation-reduction systems have been shown to be reversible* and to give definite potentials dependent on the ratio of oxidized to reduced forms, and in many cases on the hydrogen ion concentrations. The substances studied have been indigo-sulphonates, methylene blue, Bindschedler's green and a number of indophenols and safranines; † quinones and their derivatives; ‡ purines and related compounds; § azo-compounds; || ionizable free radicals of the type Ar_3C , where Ar is an aromatic group; ** semi-quinones; †† and many systems of biological importance, e.g. ascorbic acid, cytochrome, etc. ‡‡

Measurement of Oxidation-Reduction Potentials—The simplest method of determining the oxidation-reduction potential

* Clark (W. M.), *Chem. Reviews*, 1925, 2, 127; see also, International Critical Tables, Vol. VI, 1929, p. 338 for references.

† Clark, *J. Wash. Acad. Sci.*, 1920, 10, 255; Clark *et al.*, *U.S.A. Public Health Reports*, 1923, 38, 443, 666, 933, 1669; 1924, 39, 381, 804; 1925, 40, 649, 1131; 1926, Supplements No. 54, 55; 1927, No. 61, 66; 1928, No. 69, 71; 1929, No. 74; 1931, No. 92; *J. Amer. Chem. Soc.*, 1932, 54, 1228; 1933, 55, 891, 4097.

‡ Granger and Nelson, *ibid.*, 1921, 43, 1401; Conant *et al.*, *ibid.*, 1922, 44, 1382, 2480; 1923, 45, 2194; 1924, 46, 1858; 1933, 55, 3745; La Mer and Baker, *ibid.*, 1922, 44, 1954; Büllmann *et al.*, *J. Chem. Soc.*, 1925, 127, 199; Fieser *et al.*, *J. Amer. Chem. Soc.*, 1928, 50, 439, 465; 1930, 52, 4915; 1931, 53, 793; 1934, 56, 1565; 1935, 57, 491; and other references below.

§ Büllmann and Lund, *Ann. Chim.*, 1923, 19, 137; Filite, *Compt. rend.*, 1934, 198, 930; *J. Chim. physique*, 1935, 32, 1; Green, *Biochem. J.*, 1934, 28, 1550.

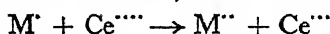
|| Büllmann and Blom, *J. Chem. Soc.*, 1924, 125, 1719.

** Conant *et al.*, *J. Amer. Chem. Soc.*, 1925, 47, 1959; 1933, 55, 3752.

†† Michaelis and Hill (E.S.), *ibid.*, 1933, 55, 1481; Michaelis, *ibid.*, 1936, 58, 873; *Chem. Reviews*, 1935, 16, 243 (for full references); Elema, *Rec. trav. chim.*, 1933, 52, 569; 1935, 54, 76.

‡‡ For accounts and references, see Hewitt, *Oxidation-Reduction Potentials in Bacteriology and Biochemistry*; Michaelis; *Oxidation-Reduction Potentials* (Eng. trans.).

is to make up a solution containing known amounts of the various forms taking part in the reversible process; a platinum electrode is inserted and the potential measured against a standard half-element. Several investigators have been unable to obtain steady potentials with platinum electrodes in certain systems and have suggested the use of mercury; * the reversible potential should be independent of the electrode material and this has been found to be the case.† Frequently some time elapses before the potential becomes constant; the constant value is then frequently considered to be the reversible value, but according to Luther ‡ this is not necessarily so. The attainment of equilibrium between ions, electrons and electrode may sometimes be expedited; Spencer and Abegg § in their study of the thallos-thallic potential found that equilibrium was reached rapidly by using a platinized platinum electrode which had just been used as either anode or cathode in the electrolysis of dilute sulphuric acid. Another method of expediting equilibrium depends on the use of a 'potential mediator' ¶ that is a substance which undergoes reversible oxidation-reduction and reaches equilibrium *rapidly*; the potential attained must be the same as that due to the main oxidation-reduction process. Consider a mixture of two ions M'' and M' say, which only reaches equilibrium slowly with an electrode, and suppose a very small quantity of a ceric salt is added; the reaction



occurs until the tendency of M' to be oxidized to M'' is exactly balanced by the tendency of Ce^{IV} to be oxidized to Ce^{III} , that is until the $M''|M'$ and $Ce^{IV}|Ce^{III}$ potentials are equal. The platinum electrode comes rapidly to equilibrium with the ceric and cerous ions, and will soon register a stable potential which is also that due to the $M'' + e \rightleftharpoons M'$ system. If the potential mediator is used in very small amounts then a negligible quantity of M' is used up and M'' formed when equilibrium is reached, and the measured potential may be regarded as the value for the original system. The first use of a potential mediator was made by Loimaranta **

* Forbes *et al.*, *J. Amer. Chem. Soc.*, 1914, 36, 2030; 1917, 39, 1140; Kiehl and Hart, *ibid.*, 1928, 50, 2337.

† Clark (W. M.) and Cohen (B.), *U.S.A. Public Health Reports*, 1923, 38, 933; Collenberg, *Z. physikal. Chem.*, 1924, 109, 353; Butler, Hugh and Hey, *Trans. Faraday Soc.*, 1926, 22, 24; Flexner and Barron, *J. Amer. Chem. Soc.*, 1930, 52, 2773; see, however, Lepper and Martin, *Biochem. J.*, 1931, 25, 45.

‡ *Loc. cit.*

§ *Z. anorg. Chem.*, 1905, 44, 379.

¶ This was first suggested by Haber, *Z. Elektrochem.*, 1901, 7, 1048. footnote.

** *Z. Elektrochem.*, 1907, 13, 33; at the suggestion of Abegg, *ibid.*, p. 34; see also Foerster and Pressprich, *ibid.*, 1927, 33, 176.

in studying the oxidation-reduction potential of arsenate-arsenite in acid solution; potassium iodide was used as the mediator, since the potential of the system iodine-iodine ions is rapidly established. Goard and Rideal* used ceric carbonate as potential mediator in some measurements of the arsenate-arsenite system in alkaline solution. Luther† has criticized the use of a potential mediator, and has shown that a definite potential is not necessarily the reversible value; the results should be independent of electrode material and should comply with the thermodynamic equation (xvi).

A method for measuring oxidation-reduction potentials has been developed in which the potential mediator is used as a titrant.‡ The pure oxidized form of an organic substance, e.g. quinone, is dissolved in a solution of known hydrogen ion concentration and known amounts of a reducing solution, e.g. titanous chloride or sodium hydrosulphite, are added and the solution stirred; the potential of a platinum electrode immersed in the reacting solution is measured after each addition. At a certain point the potential becomes suddenly much more negative and then reduction is complete (cf. p. 349); the quantity of reducing solution added is at this point equivalent to the whole of the organic compound originally present. From the amounts of reducing agent added at various stages the corresponding ratio of oxidized form [Q] to reduced form [H_2Q] may be calculated, and the normal oxidation-reduction potential determined from the approximate equation

$$\pi = \pi_0 + \frac{RT}{2F} \ln \frac{[Q]}{[H_2Q]} + \frac{RT}{F} \ln [H'] \quad (xxii)$$

The results obtained in this way agree with those obtained by making up mixtures of known amounts of Q and H_2Q ; hence the presence of the inorganic reducing agent does not affect the results. It has been shown by La Mer and Baker§ that the same values may be obtained by starting with the reduced form H_2Q and titrating it with an oxidizing agent, e.g. potassium dichromate; potential mediators and coupled reactions may thus be used without introducing serious errors.||

* *Trans. Faraday Soc.*, 1924, 19, 740.

† *Loc. cit.*

‡ Clark, *loc. cit.*, 1923; Conant *et al.*, *loc. cit.*, 1922; see also, Fieser, *J. Amer. Chem. Soc.*, 1930, 52, 4915 for method suitable for unstable substances.

§ *Loc. cit.*

|| For a coupled-reaction method involving the use of an optically active quinone as oxidizing agent, see Hunter and Kvalnes, *ibid.*, 1932, 54, 2869; 1934, 56, 667, 670, 2478, 2487; for a photo-electric method in which coloured oxidizing substances are employed, see Holst, *Z. physikal. Chem.*, 1935, 175, 99.

importance, as oxidations and reductions are never carried out at infinite dilution but in the presence of acid, alkali or neutral salts; they are, however, not definite constants for the *system*, but only properties of the particular solutions being studied.

In order to determine the true oxidation-reduction potential of a system it is necessary to allow for the ionic strength of the medium, and the consequent departure of the activity coefficients from unity, for possible hydrolysis of the salts and for complex ion formation, which would affect the actual concentration of the ions present, and finally for liquid junction potentials. When the appropriate corrections are made the standard potential for the system being studied has a definite value, irrespective of the nature of the solutions used in the measurements.* In Table XLIX is given a list of standard oxidation-reduction potentials: a number of these are only approximate because of the uncertainty in applying the corrections indicated above.†

TABLE XLIX
STANDARD OXIDATION-REDUCTION POTENTIALS (25°)

Ag ⁺ , Ag ⁺ (at 0°)	+ 1.91	Fe ³⁺ , Fe ²⁺	+ 0.772
Co ³⁺ , Co ²⁺	+ 1.817	Mo(CN) ₈ ³⁻ , Mo(CN) ₈ ⁴⁻	+ 0.726
Pb ⁴⁺ , Pb ²⁺	+ 1.75	MnO ₄ ⁻ , MnO ₄ ²⁻	+ 0.664
Mn ³⁺ , Mn ²⁺	+ 1.642	Fe(CN) ₆ ³⁻ , Fe(CN) ₆ ⁴⁻	+ 0.356
Ce ⁴⁺ , Ce ³⁺	+ 1.60	Cu ²⁺ , Cu ⁺	+ 0.16
Mn ³⁺ , Mn ²⁺	+ 1.576	Ti ³⁺ , Ti ²⁺	+ 0.06
MnO ₄ ⁻ + 8H ⁺ , Mn ²⁺	+ 1.45	Sn ⁴⁺ , Sn ²⁺	- 0.15
Ti ³⁺ , Ti ²⁺	+ 1.221	V ³⁺ , V ²⁺	- 0.2
IO ₃ ⁻ + 6H ⁺ , $\frac{1}{2}$ I ₂	+ 1.197	Ti ³⁺ , Ti ²⁺	- 0.37
Hg ²⁺ , Hg ₂ ²⁺	+ 0.905	Cr ³⁺ , Cr ²⁺	- 0.412

Use of Oxidation-Reduction Potentials—From a knowledge of the standard oxidation-reduction potentials it is possible to calculate, with the appropriate form of equation (xvi), the potential of any mixture of oxidized and reduced forms; for approximate purposes it is sufficient to substitute concentrations for activities.

* For the methods used to make the corrections, see the references immediately below.

† For recent studies of oxidation-reduction systems, see: **argentic-argentous**: Noyes (A. A.) and Kossiakoff, *J. Amer. Chem. Soc.*, 1935, 57, 1238; **ceric-cerous**: Kunz, *ibid.*, 1931, 53, 98; Noyes and Garner (C. S.), *ibid.*, 1936, 58, 265; **thallic-thallous**: Partington and Stonehill, *Trans. Faraday Soc.*, 1935, 31, 1357; Sherrill and Haas, *J. Amer. Chem. Soc.*, 1936, 58, 952; Noyes and Garner, *ibid.*, p. 1268; **mercuric-mercurous**: Popoff *et al.*, *ibid.*, 1931, 53, 1195; **ferric-ferrous**: *Idem.*, *ibid.*, 1929, 382; 1931, 53, 1643; Bray and Hershey, *ibid.*, 1934, 56, 1889; Schumb and Sweetser, *ibid.*, 1935, 57, 871; **ferro-ferricyanide**: Kolthoff and Tomsicek, *loc. cit.*, 1935; **molybdo-molybdicyanide**: *idem.*, *loc. cit.*, 1936; **cupric-cuprous**: Fenwick, *J. Amer. Chem. Soc.*, 1926, 48, 860; **stannic-stannous**: Huey and Tartar, *ibid.*, 1934, 56, 2585.

Some of the results obtained in this way are plotted in Fig. 24. It is seen that in every case the potential rises rapidly at first as the amount of oxidized form is increased: this is due to the fact that when the proportion of the latter is small a relatively small increase in quantity brings about a large increase in the ratio of

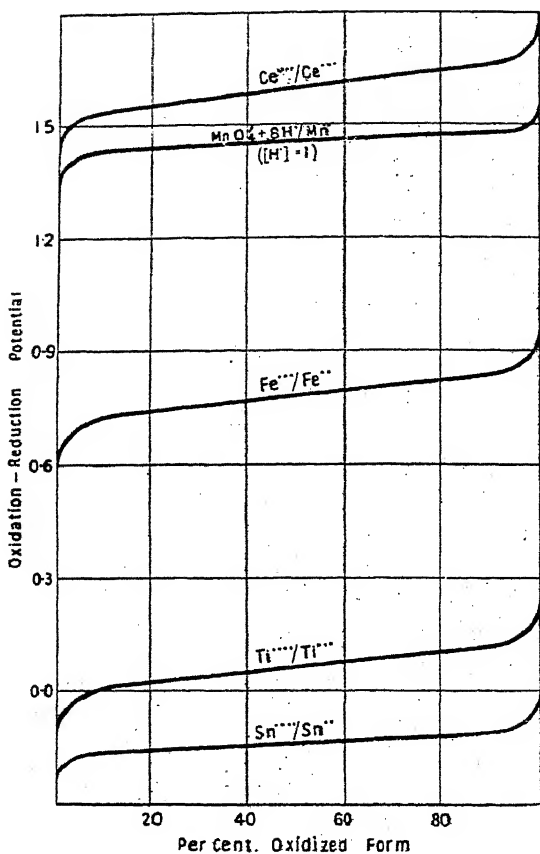


FIG. 24.—Oxidation-reduction potentials of mixtures of oxidized and reduced forms in various ratios

oxidized to reduced forms, and it is this ratio which determines the potential. As the amounts of oxidized and reduced states become of the same order, the potential changes only slowly, since an increase or decrease in either brings about little change in the ratio. Solutions in this condition are said to be 'poised';* this

* Clark *et al.*, *U.S.A. Public Health Reports*, 1923, 38, 443; 1927, Suppl. No. 61.

is the equivalent of the term 'buffered' as applied to changes of hydrogen ion potential. It will be noted that the slope of this portion of the curve in Fig. 24 depends on the value of N in equation (xvi), that is on the difference in charge between oxidized and reduced states: the greater this difference the less the slope of the curve and the more effectively is the solution poised. When the system consists almost exclusively of the oxidized form then, as at the other extreme, the potential again changes rapidly as seen at the right-hand side of the figure.

If a solution consisting entirely of a reduced form, e.g. ferrous ions, is oxidized by a suitable reagent, e.g. as in the titration by permanganate, the potential follows the appropriate curve, viz. $\text{Fe}^{+++}/\text{Fe}^{++}$, from left to right. As the oxidation approaches completion, however, the shape of the curve may be influenced by the nature of the oxidizing agent employed. The complete potential-titration curve can be obtained by plotting the curves for the two systems, namely that being oxidized and that of the oxidizing agent, side by side and joining them by a tangent. If the two curves are far apart, that is to say the standard potentials for the two systems differ by at least 0.3 volt, as with a ferrous salt and dichromate or permanganate, the oxidation of the former is virtually complete when the equivalent amount of the latter has been added, and at the equivalence-point the potential rises rapidly. This is analogous to the behaviour observed in the titration of a strong acid by a strong base. Should the two curves be fairly close together, however, then there is no sharp change of potential at the equivalence-point, and it is obvious from the shape of the pair of curves that the solution will contain appreciable amounts of the oxidizing agent which have not reacted even before oxidation of the substance being titrated is complete: the curve is analogous to that obtained in the neutralization of a weak acid by a weak base, and such pairs of systems could not be used in analytical work.*

Oxidation-Reduction Indicators—Many organic dyestuffs, in combination with the corresponding colourless leuco-compounds obtained on reduction, yield reversible oxidation-reduction systems which are capable of being used within limits as indicators of oxidation-reduction potentials. Mixtures of the oxidized and reduced forms in different proportions will have different depths of colour, and every depth corresponds to a definite oxidation-reduction potential. Each indicator is applicable only over a definite range of potentials in the vicinity of its own standard potential; outside this range the colour will be indistinguishable from that of the completely oxidized or reduced form. If a small amount of such an appropriate indicator is placed into an oxidation-reduction

* For a further quantitative consideration of this subject, see p. 394.

system, the former, acting as a potential mediator, will enter into an equilibrium in which its oxidation-reduction potential is the same as that of the system under examination: from the colour of the solution the value of its potential may be estimated. The indicators used must, of course, be standardized by actual electrode potential measurements* or by means of suitable 'poised' solutions.† Most of the oxidation-reduction indicators employed are either quinonoid in the oxidized form, or are analogous in so far as two atoms of hydrogen are required to bring about the reduction of each gm. mol.; ‡ the potential then depends on the hydrogen ion concentration in the manner shown by equations (xxi) or (xxii). It is evident, therefore, that in the use of oxidation-reduction indicators the pH of the solution must be known, for it is this, in addition to the depth of colour, which corresponds to the ratio $[Q]/[H_2O]$, that determines the actual potential. In the deduction of equation (xxi) the possibility of the presence of acidic or basic groups in the oxidized and reduced forms has been ignored: this is justifiable as long as the corresponding dissociations are small, but when they become appreciable, viz. basic functions in acid solution, and acidic functions in alkaline media, the simple equation is no longer obeyed (cf. p. 381). The actual equation connecting the potential with the hydrogen ion concentration and the ratio of oxidized to reduced forms also includes the dissociation constants of the various acidic and basic groups.§

It can be seen that if equation (xxi) is applicable, the potential of a given oxidation-reduction system of the quinone-hydroquinone type against that of a hydrogen gas electrode in the *same solution*, depends only on the ratio of oxidized to reduced forms and the constant π_0 , and is independent of the hydrogen ion concentration. This means that the oxidation-reduction electrode is itself equivalent to a hydrogen electrode operating at a gas pressure p , and equation (xxi) may be written in the alternative form

$$\pi = \frac{RT}{2F} \ln \frac{1}{p} + \frac{RT}{F} \ln a_H \quad \dots \quad (xxia)$$

The hypothetical pressure p , and consequently a term r_H , defined as $-\log p$, thus involves both π_0 and the ratio of oxidized to reduced forms, and is thus a measure of the oxidation intensity of the system independent of the pH of the medium.|| The higher

* Clark *et al.*, *loc. cit.*

† Hirsch and Rüter, *Z. anal. Chem.*, 1926, 69, 193.

‡ For exceptions see, Michaelis and Friedheim, *J. Biol. Chem.*, 1931, 91, 355; Elema, *Rec. trav. chim.*, 1933, 52, 569; Michaelis, *Chem. Reviews*, 1935, 16, 243; Remick, *J. Amer. Chem. Soc.*, 1936, 58, 733.

§ Clark, *loc. cit.*, 1923.

|| *Idem.*, *U.S.A. Public Health Reports*, 1923, 38, 666.

the value of r_H the greater is the oxidizing power of a given system. Under such conditions that it is necessary to include acidic and basic dissociation constants in the equation for the electrode potential, equation (xxia) does not apply, and r_H is not independent of the pH of the solution; it is then no longer a satisfactory measure of oxidation intensity, and must be used with caution.* The term r_H is, however, often employed in the study of biological systems where the pH is generally in the vicinity of that of the neutral point.† In addition to the application of r_H to define the oxidation-reduction potential of a given solution, it is also used in connection with an oxidation-reduction indicator to state the range of potential over which it is applicable, just as the range of an acid-base indicator is expressed in terms of pH units (Table XL). The middle of the r_H range corresponds to the intermediate colour, that is with equal amounts of oxidized and reduced forms, and consequently it is equivalent to the standard potential of the indicator at the hydrogen ion concentration of the solution.‡ In general, therefore, an oxidation-reduction indicator changes colour appreciably at a potential in the vicinity of its standard potential at the pH of the medium.

Oxidation-reduction indicators which are of practical value may be divided roughly into two categories: there are those of relatively low potential, viz. $+0.3$ to -0.4 volt at pH 7, used in biological work, and those of higher potential, greater than 0.7 volt, which are employed in volumetric analysis. The former consist mainly of indophenols, indigo-sulphonates, safranines and substituted dipyrilidium chlorides ('viologens'), and are too unstable to be used for analytical purposes.§ The interest in the application of oxidation-reduction indicators in volumetric work has followed on the discovery that the familiar colour change undergone by diphenylamine on oxidation can be used to detect the end-point in the titration of ferrous ions by dichromate.|| Diphenylamine, generally in the form of its soluble sulphonc acid, at first undergoes irreversible oxidation to diphenylbenzidine, and it is this substance which with diphenylamine violet, its oxidation product, gives a reversible oxidation-reduction system with a standard potential of about 0.75 volt in acid solution.** If phosphoric acid or a fluoride is added to suppress the ferric ion concentration, then it is only when oxidation of the ferrous salt is complete that the potential

* *Idem.*, U.S.A. Hyg. Lab. Bull., 1928, No. 151, Suppl. notes, p. 342.

† Michaelis, *Oxydations-Reductions Potentiale*, 1933.

‡ The standard potential at a given hydrogen ion concentration is equal to $\pi_0 + RT/F \ln a_H$, and is often represented by π_0' and E_0' .

§ For full references, see review article by Glasstone, *Ann. Reports Chem. Soc.*, 1934, 31, 305.

|| Knop, *J. Amer. Chem. Soc.*, 1924, 46, 263.

** Kolthoff and Sarver, *ibid.*, 1930, 52, 4179.

risers sufficiently to exceed that requisite for the production of diphenylamine violet. Since the standard $\text{Fe}^{3+}/\text{Fe}^{2+}$ potential is 0.77 volt it is evident that if the ferric ion concentration is not kept low by complex formation the colour change, from green to violet, will be gradual and no satisfactory end-point will be detected. Theoretically, a satisfactory oxidation-reduction indicator for titrimetric work should have a standard potential lying on the almost vertical portion of the oxidation-reduction potential curve (see p. 349): the colour change will then take place sharply when oxidation of the substance titrated is complete. In the ferrous ion-dichromate or ferrous ion-ceric ion titrations the potential changes rapidly between 0.9 and 1.2 volt, or 0.9 and 1.5 volt respectively: a suitable indicator, not requiring the suppression of the ferric ions, is the *o*-phenanthroline ferrous ion (intense red) which with the corresponding ferric ion (pale blue) has a standard potential of about 1.1 volt.* Phenylanthranilic acid, standard oxidation-reduction potential 1.08 volt, has been suggested for the same purpose.† These and other indicators are particularly useful for volumetric titrations with ceric sulphate, with dichromate and with very dilute solutions of permanganate as oxidizing agents.‡

Irreversible and Inaccessible Reduction Potentials—

There are many oxidation-reduction reactions which are not reversible thermodynamically, or else they come to equilibrium so slowly that their potentials are inaccessible. Goard and Rideal § have suggested the use of a 'controlled' oxygen electrode to obtain an approximate comparison of the reducing intensity of inaccessible systems. The actual electrode used was made by immersing a clean piece of platinum wire for three-quarters of an hour in a solution consisting of 90 c.c. of a borate solution of pH 9, and 10 c.c. of *N*/10-potassium permanganate; the wire was washed and immediately inserted into the oxidation-reduction system being studied. The potential of this electrode rose rapidly to a maximum and then fell; the maximum value was taken as giving a comparative measure of the oxidation-reduction potential of the system. Methylene blue has been used as potential mediator in systems

* Walden (G. R.), Hammett and Chapman (R. P.), *ibid.*, 1931, 53, 3908; 1933, 55, 2649; for review, see Walden and Edmonds, *Chem. Reviews*, 1935, 16, 81.

† Syrokonsky and Stiepin, *J. Amer. Chem. Soc.*, 1936, 58, 928.

‡ For review of oxidation-reduction indicators and their applications, see Glasstone, *loc. cit.*; more recent work is described by Sarver *et al.*, *ibid.*, 1935, 57, 329; *Ind. Eng. Chem. (Anal.)*, 1935, 7, 271; Straka and Oesper, *ibid.*, 1934, 6, 465; Willard and Young (P.), *ibid.*, 1935, 7, 57; and references given immediately above.

§ *Loc. cit.*; see also Remington and Trimble, *J. Physical Chem.*, 1929, 33, 424.

involving glucose in order to hasten the attainment of equilibrium, or to give a comparative reduction potential.*

Conant and his collaborators† have determined the apparent oxidation or reduction potentials of irreversible or unstable systems involving organic compounds; these potentials are defined as the 'normal potential of the *reversible* system that will just cause appreciable reduction (20–30 per cent. in 30 minutes)'—or oxidation—of the compound under consideration. The values obtained may be regarded at least as comparative.

Ionization in Stages—Metals yielding two positive ions, e.g. copper, lead, iron and mercury, have two electrode potentials depending on whether the metal is in equilibrium with ions of lower or higher valency. In the general case of a metal M able to form cations $M^{n_1\oplus}$ and $M^{n_2\oplus}$, where the valency $n_2 > n_1$, let π_1 and π_2 represent the *standard* electrode potentials for the systems $M | M^{n_1\oplus}$ and $M | M^{n_2\oplus}$, respectively; the oxidation–reduction potential of the two ions is represented by π_0 . One gm. atom of metal may be transferred from solid metal M into a solution of $M^{n_1\oplus}$ ions at unit activity with the expenditure of $n_1\pi_1 F$ volt-coulombs of energy; the same final result may be achieved by transferring the gm. atom of metal into a solution of $M^{n_2\oplus}$ ions at unit activity, and then oxidizing the gm. ion to $M^{n_1\oplus}$ ions at unit activity. The electrical energy involved in this alternative process is $n_1\pi_1 F + (n_2 - n_1)\pi_0 F$. The two work terms must be identical; hence

$$n_2\pi_2 = n_1\pi_1 + (n_2 - n_1)\pi_0 \quad . \quad . \quad . \quad (xxvi)$$

$$\pi_2 = \frac{n_1}{n_2}\pi_1 + \frac{n_2 - n_1}{n_2}\pi_0 \quad (xxvii)$$

In many cases it is not possible to measure π_1 directly, whereas π_1 and π_0 can generally be determined experimentally; by means of equation (xxvii) π_2 may be calculated. For a lead electrode $Pb | Pb^{++}(a = 1)$ is -0.12 volt; for $Pb^{++} | Pb^{+++}$ π_0 is 1.75 volt, and so the standard potential for $Pb | Pb^{+++}$, which cannot be measured directly, is calculated as $+0.81$ volt. If the metal M is dipped into a solution containing the two cations, an equilibrium between M , $M^{n_1\oplus}$ and $M^{n_2\oplus}$ will be established:



This reaction will occur in one direction or another until the concentrations of the ions are such that all three possible electrode

* See, for example, Wurmser and Geloso, *Compt. rend.*, 1928, 186, 1842.

† *J. Amer. Chem. Soc.*, 1923, 45, 1047; 1924, 46, 1254; 1926, 48, 2468, 3178; 1930, 52, 407; *Chem. Reviews*, 1926, 3, 1; *J. Physical Chem.*, 1924, 28, 1096; see also, Fieser, *J. Amer. Chem. Soc.*, 1930, 52, 5204.

potentials are identical; only then is the system in equilibrium. Thus a lead electrode will be in equilibrium with plumbous and plumbic ions at 18°, when

$$-0.12 + 0.029 \log [\text{Pb}^{++}]_e = 0.81 + 0.0145 \log [\text{Pb}^{+++}]_e,$$

where $[\text{Pb}^{++}]_e$ and $[\text{Pb}^{+++}]_e$ are the equilibrium concentrations, assumed to be proportional to the respective activities. From this equation it is found that

$$\frac{\sqrt{[\text{Pb}^{+++}]_e}}{[\text{Pb}^{++}]_e} = 10^{-32} \text{ (approx.)}$$

It is clear, therefore, that only an extremely minute concentration of plumbic ions can be present in any stable system containing metallic lead; if plumbic ions are in excess of this amount they will react with the lead to form plumbous ions.* In the case of mercury the equilibrium is expressed by the relation $[\text{mercurous ions}]/[\text{mercuric ions}] = 120$; hence appreciable concentrations of mercuric ions can co-exist with metallic mercury.

Electrode Potentials with Non-Aqueous Solvents †—A number of measurements have been made of the *E.M.F.*'s of concentration cells with non-aqueous solutions and fundamentally the behaviour seems to be the same as for aqueous solutions. Although some doubt was at one time cast on the applicability of the Nernst equation,‡ it is now generally accepted that the formula is quite satisfactory, and any considerable deviations are to be attributed to the formation of complexes between solvent and solute.§ The *E.M.F.* of a concentration cell involving a uni-univalent electrolyte, reversible with respect to the cation, e.g. $\text{Ag} | \text{AgNO}_3(c_1) \cdot \text{AgNO}_3(c_2) | \text{Ag}$, may be written in the form

$$E = n_a \frac{RT}{nF} \ln \frac{a_1}{a_2} = n_a \frac{RT}{nF} \ln \frac{\gamma_1 c_1}{\gamma_2 c_2}$$

where a_1 and a_2 are the activities of the salt in the two solutions. Since the activity coefficients have not been known, the equation has been used in the approximate form in which γ_1 and γ_2 have been replaced by α_1 and α_2 , the conductance ratios Λ_1/Λ_0 and

* Cf. Glasstone, *J. Chem. Soc.*, 1922, 121, 1469.

† For further details consult Walden, *Elektrochemie nichtwässriger Lösungen*, 1924; Müller, *Ahren's Sammlung Chem. und Chem.-tech. Vorträge*, 1924, 27, 243.

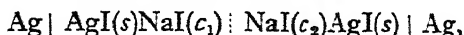
‡ Kahlenberg, *J. Physical Chem.*, 1900, 4, 709; Wilson, *Amer. Chem. J.*, 1906, 36, 78.

§ Abegg and Neustadt, *Z. physikal. Chem.*, 1909, 69, 416; Gibbons and Getman, *J. Amer. Chem. Soc.*, 1914, 36, 1630 (full references); Grant and Partington, *Trans. Faraday Soc.*, 1923, 19, 414; Koch, *J. Chem. Soc.*, 1928, 524; Müller (R.), *Monatsh.*, 1933, 63, 317; Costeanu, *Compt. rend.*, 1933, 197, 1113.

Λ_1, Λ_2 , respectively; hence the Nernst equation as often used is

$$E = n_a \frac{RT}{nF} \ln \frac{\Lambda_1 c_1}{\Lambda_2 c_2}.$$

In order to verify this relationship it is necessary to know the transport number of the anion and the conductivities of the two solutions; accurate data are not always available, but where they have been obtained the equation has been found to be applicable, provided the solutions are dilute and no compound formation occurs between solvent and solute. Exact agreement would not in any case be expected unless by chance α_1/α_2 and γ_1/γ_2 were equal; as a rule the range of concentrations studied is not very great, and so the ratios do not differ considerably.* It has been found that the Nernst equation is applicable to concentration cells reversible with respect to the anion, e.g. of the type



both with † and without ‡ transport. The *E.M.F.* of a cell consisting of two amalgams has been found to be independent of the nature of the solvent and the concentration of the solute.§ Oxidation-reduction systems in non-aqueous solutions give potentials in agreement with the thermodynamic equation, provided allowance be made for the formation of complex ions in certain cases.||

Single Potentials in Non-Aqueous Solutions—The determination of single potentials in non-aqueous solutions has hitherto been characterized by marked uncertainties. A number of results have been published,** but as a rule these are very divergent; the reported standard potentials in methyl alcohol of silver vary from 0.76 to 0.91, and those of copper from 0.27 to 0.43. The uncertainties are also shown in the attempts made to correlate the normal potential of a metal in a particular solvent with the dielectric constant of the solvent. Some authors consider there is a parallelism between these quantities,†† although the suggested relation is not

* See, for example, Nonhebel and Hartley, *Phil. Mag.*, 1925, 50, 729.

† Isaacs and Partington, *Trans. Faraday Soc.*, 1929, 25, 53; see also Brodsky, *Z. physikal. Chem.*, 1926, 121, 1; Afanasiev, *Z. Elektrochem.*, 1929, 35, 220; *J. Amer. Chem. Soc.*, 1930, 52, 3477.

‡ Partington and Simpson, *Trans. Faraday Soc.*, 1930, 26, 625.

§ Cady, *J. Physical Chem.*, 1898, 2, 551.

|| Abegg and Neustadt, *Z. Elektrochem.*, 1909, 15, 264; Partington and Skeen, *Trans. Faraday Soc.*, 1934, 30, 1062; 1936, 32, 975.

** Kahlenberg, *loc. cit.*; Koch, *J. Chem. Soc.*, 1928, 269; Buckley and Hartley, *Phil. Mag.*, 1929, 8, 320, for references.

†† Luther, *Z. physikal. Chem.*, 1896, 19, 529; Baur, *Z. Elektrochem.*, 1906, 12, 725; Mortimer and Pearce, *J. Physical Chem.*, 1917, 21, 275; Ghosh *et al.*, *J. Ind. Chem. Soc.*, 1924, 1, 189; Brodsky, *Z. physikal. Chem.*, 1924, 121, 26.

always the same; others, however, find no connection between electrode potential and dielectric constant.* In any case the order of the electrode potential series does not appear to be the same in all solvents.† According to modern views (p. 361) the factor influenced by the solvent is the free energy of solvation of the ions, and this is related to the dielectric constant by the Born equation (p. 51), provided chemical reaction between the ion and solvent does not occur. There is some evidence that for solvents of a similar type, e.g. water and alcohols, the standard potentials and dielectric constant are connected, at least, approximately, in the expected manner; when there is chemical solvation, however, discrepancies are observed.‡

In the early work electrode potentials were measured against a standard electrode containing an aqueous solution, in order that the results might be reduced to a generally accepted scale. In this way serious errors were introduced, since the potentials between two different liquids are probably large; their magnitudes are unknown, however, and can neither be calculated nor eliminated in the usual manner. Further, there is always a risk of contamination of the non-aqueous electrolyte by traces of water; these often produce an appreciable effect on the activities and mobilities of the ions.§ Even if the potentials were determined with accuracy, which seems improbable, there has been no definite information concerning the activity of the electrolyte in the non-aqueous solvent; hence the standard potentials could not in any case be reliable. The only satisfactory method of dealing with this problem is to consider each solvent as an independent system, and not to try to connect the results with those obtained in aqueous solutions; a definite attempt in this direction, using methyl and ethyl alcohols as solvents, has been made by Hartley and his collaborators.|| Since in this work the same liquid is used throughout the cell the usual formulæ for calculating liquid junction potentials are applicable; thus, various forms of the Henderson equation (p. 315) may be used according to the existing conditions.

* Koch, *loc. cit.*

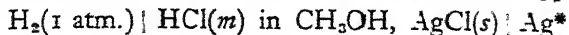
† Gates, *J. Physical Chem.*, 1911, 15, 97; Ghosh, *ibid.*, 1915, 19, 720; see, however, *infra*.

‡ Koch, *J. Chem. Soc.*, 1930, 1551; 1931, 1138; Macfarlane and Hartley (H.), *Phil. Mag.*, 1935, 20, 611; Drewski, *Rocz. Chem.*, 1934, 14, 865; Pleskov and Monossohn, *Acta Physicochim. U.R.S.S.*, 1935, 2, 621.

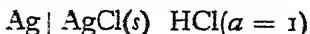
§ Nonhebel and Hartley, *loc. cit.*; Murray-Rust and Hartley, *Proc. Roy. Soc.*, 1930, 126 A, 84.

|| *loc. cit.*, 1929, 1935; *Phil. Mag.*, 1932, 13, 425; see also Danner, *J. Amer. Chem. Soc.*, 1922, 44, 2832; Harned and Fleysher, *ibid.*, 1925, 47, 82; Scatchard, *ibid.*, p. 2098. For observations with liquid ammonia as solvent, see Pleskov and Monossohn, *J. Physical Chem. U.S.S.R.*, 1933, 4, 696; *Acta Physicochim. U.R.S.S.*, 1935, 2, 615.

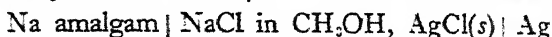
By measurements of the *E.M.F.*'s of cells of the type



at different concentrations of acid and extrapolating in a manner similar to that used for aqueous solutions (p. 363) the *E.M.F.* of the cell with acid at unit activity was obtained. From this the standard potential on the hydrogen scale of



in methyl alcohol was determined; using other measurements of the same cell containing 0.1*N*-HCl, the potential of the electrode $\text{Ag} | \text{AgCl}(s) | 0.1\text{N-HCl}$ in CH_3OH , was found to be +0.0711 volt and the activity of the acid 0.0461. Since measurements of the cell



did not give satisfactory results for the activity of sodium chloride solutions,[†] it was assumed that in 0.1*N*-solutions the activities of sodium chloride and hydrochloric acid are equal. The potential of the electrode $\text{Ag} | \text{AgCl}(s) | 0.1\text{N-NaCl}$ in CH_3OH is then taken as +0.0711, and used for reference purposes; the electrode $\text{Hg} | \text{Hg}_2\text{Cl}_2(s) | 0.1\text{N-NaCl}$ was compared with the former and also used as a standard. The potentials of half-elements involving various metals can thus be measured with reasonable accuracy, and allowance made for liquid junction potentials, if the appropriate transport numbers are known. If the activity coefficients of the electrolyte, from freezing-point or other measurements, are not available, they may be calculated approximately by means of the Debye-Hückel equation. For univalent metals, salts of univalent anions are chosen which are known, from conductance experiments, to behave as strong electrolytes in the particular solvent; the activity coefficient is assumed to be the same as that of hydrochloric acid in dilute solution at the same concentration. From the electrode potential and the activity of the electrolyte the value of the standard potential may be calculated. In order to determine the standard potentials of halogens use has been made of the fact that the *E.M.F.* of the cell $\text{Ag} | \text{AgX}(s) | \text{electrolyte} | \text{X}_2$, where X is a halogen, is a measure of the free energy of formation of the silver halide, and so is independent of the nature of the electrolyte and the solvent. The value is known for aqueous solutions, or may be calculated from the equation

$$E = \pi_{\text{Ag}} - \pi_{\text{X}} + \frac{RT}{F} \ln (a_{\text{Ag}^+} \times a_{\text{X}^-})$$

(p. 369), since the standard potentials of silver and the halogen are known and the solubility product is available. For the non-aqueous

* Nonhebel and Hartley, *loc. cit.*

† Wolfenden *et al.*, *Trans. Faraday Soc.*, 1927, **23**, 491.

solution π_{Ag} is known from measurements on the $\text{Ag}|\text{AgNO}_3$ electrode, and the activity solubility product of the halides can be determined from the potential of the $\text{Ag}|\text{AgX(s)}|\text{NaX}$ electrode (p. 368); hence the standard potential of the halogen may be evaluated. Proceeding in this manner the values given in Table L have been obtained for methyl and ethyl alcohol solutions; the potentials in aqueous solutions are those given by Buckley and Hartley for purposes of comparison.

TABLE L
STANDARD ELECTRODE POTENTIALS

Element.	Ethyl Alcohol.	Methyl Alcohol.	Water.
Lithium . . .	- 3.04	- 3.095	- 2.958
Sodium . . .	- 2.66	- 2.728	- 2.7125
Thallium . . .	- 0.343	- 0.379	- 0.3363
Cadmium . . .	—	- 0.258	- 0.398
Hydrogen . . .	0	0	0
Copper . . .	—	+ 0.490	+ 0.345
Silver . . .	+ 0.749	+ 0.764	+ 0.7995
Iodine . . .	+ 0.305	+ 0.357	+ 0.5357
Bromine . . .	+ 0.777	+ 0.837	+ 1.0659
Chlorine . . .	+ 1.048	+ 1.116	+ 1.3594

Although there may be a potential difference between a hydrogen electrode at unit activity in water and in an alcohol, apart from liquid phase potentials, the values given in Table L may be regarded as comparable. It is interesting to note that the order of the potentials is almost the same in the three solvents; copper and cadmium are somewhat anomalous, but this is probably to be accounted for by the uncertain activity coefficients. The method used for the alcohols has been described in detail, as a similar procedure, with suitable modifications, will no doubt be adopted in the study of potentials in other solvents; such a study is an essential preliminary to a satisfactory elucidation of the problem of the origin of electrode potential, although it is doubtful if a complete solution will be available until absolute potentials are known with some certainty.

The Mechanism of the E.M.F.—It has been assumed that the *E.M.F.* of a cell is made up of the potential differences at metal-liquid and at liquid-liquid interfaces, but any difference of potential at the surface of separation of two metals has been neglected. In a concentration cell, involving identical electrodes, this factor must be zero, but in other cells the metal contact, or Volta, potential may be appreciable. It had been observed by Volta* that if two metals, held by insulating handles, are brought together one is positively and the other negatively charged on

* *Annales de Chim.*, 1801, 40, 225.

separation; a difference of potential must, therefore, act across the junction. According to Volta the liquid electrolyte in a galvanic cell tends to equalize the potentials of the two metals; as a consequence a flow of current results in an attempt to maintain the potential difference when the electrodes are connected by a wire. This theory—that the *E.M.F.* of a cell was due mainly to the metal contact potential difference—was largely supported in the past century.*

The measurements of Ayrton and Perry † indicated that a large proportion of the *E.M.F.* of a Daniell cell existed at the zinc-copper interface; these authors, however, considered that this contact potential was really caused by chemical action, e.g. between metal and oxygen, at the moment of breaking contact, ‡ and that the *E.M.F.* was due almost entirely to the chemical energy of the reaction occurring in the cell. This view had already obtained support from Faraday's discovery that a given electric current always produced equivalent chemical action, and from the agreement of heats of reaction calculated from *E.M.F.* measurements, using the Gibbs-Helmholtz equation, with the thermochemical values. It was further strengthened by Nernst's theory of the mechanism of electrode processes, which appeared to be in excellent agreement with observed facts. The only difference of potential between two metals was considered to be the very small one causing the Peltier effect, i.e. increase of temperature at the junction of two metals when current is flowing. Kelvin § showed, however, that the Peltier effect was proportional to the temperature coefficient of the contact potential, and not to the potential itself.

Electron Affinity—Until recently the Volta effect was neglected in electrochemical work, but as the result of investigations on thermionic emission and the photoelectric effect in high vacua it has been shown that every metal possesses a characteristic property called the 'thermionic work function', or 'electron affinity', ϕ ; it is expressed in volts and when multiplied by the electronic charge gives a measure of the work necessary to remove an electron from the metal surface in vacuo. || If two metals with different electron affinities are brought into contact, electrons will pass spontaneously from the metal with the smaller electron affinity to the one with the larger, with the result that a contact difference of potential, or Volta effect, is produced. The value of this potential

* See Kelvin, *Phil. Mag.*, 1898, 46, 82.

† *Proc. Roy. Soc.*, 1878, 27 A, 1916; *Phil. Trans.*, 1880, 171, 15

‡ See Lodge, *Brit. Assoc. Rep.*, 1884, 464; *Phil. Mag.*, 1900, 49, 351.

§ *Loc. cit.*

|| Langmuir, *Trans. Amer. Electrochem. Soc.*, 1916, 29, 125; Dushman and Millikan, *Phys. Rev.*, 1921, 18, 241; Rice, *Science Progress*, 1922, 16, 362.

must be equal to the difference between the electronic work functions, i.e. $\phi_A - \phi_B$, when two metals A and B are in contact. At present only approximate values of ϕ are available, as the photoelectric and thermionic effects, from which they are calculated, are very sensitive to the presence of impurities and other disturbing factors. The results given in Table LI show that the Volta effect might be of considerable magnitude.

TABLE LI
THERMIONIC WORK FUNCTION (VOLTS)

Metal.	ϕ	Metal.	ϕ
Potassium	1.45	Lead	3.4
Sodium	1.82	Cadmium	3.5
Lithium	2.3	Iron	3.7
Calcium	2.6	Tin	3.8
Magnesium	2.7	Copper	4.0
Aluminium	3.0	Silver	4.1
Zinc	3.4	Platinum	4.4

Butler* has shown that the contact potential between any metal M and platinum, calculated from the thermionic work functions, is almost equal to the measured *E.M.F.* of the cell $M | MX \text{ aq. } || H^+ | H_2(Pt)$, in which a platinum-M junction is involved; the result suggests that contact potential is mainly responsible for the *E.M.F.* of a galvanic cell. This opinion is not contrary to the concept of the equivalence of the *E.M.F.* and the free energy of the reaction occurring in the cell, but it merely implies that most of the energy is involved in transferring electrons from one metal to the other. Corbino† favours Butler's view, but on the other hand Heyrovský (*vide infra*) considers that the Volta potential constitutes a small proportion of the *E.M.F.* of a cell. Rideal‡ has suggested that the Volta effect is the cause of the flow of electrons which results in the production of potential differences at the two metal-liquid interfaces; the seat of the *E.M.F.* of a galvanic cell is believed to be at these interfaces. More recently the subject has been treated by the methods of quantum mechanics by Gurney,§ who has concluded that it is the Volta effect, or the difference in the thermionic work functions at the metal-metal contact, which is mainly responsible for the *E.M.F.* of a reversible cell. In addition, however, the 'interface potentials', between metal and solution, contribute something to the total.|| Although there is still some difference of opinion concerning the origin and seat of the

* *Phil. Mag.*, 1924, 48, 927.

† *Ibid.*, 1927, 4, 436.

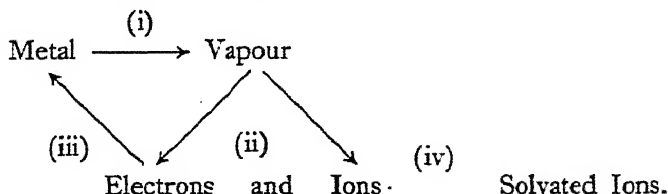
‡ *Trans. Faraday Soc.*, 1924, 19, 667.

§ Gurney, *Proc. Roy. Soc.*, 1932, 136 A, 378; see also, Fowler, *Trans. Faraday Soc.*, 1932, 28, 368.

|| For measurements, see Bancroft, *J. Physical Chem.*, 1936, 40, 1201.

E.M.F. of a galvanic cell, it must be admitted that the accepted standard electrode potential of a metal may not give merely the difference of potential between the metal and a solution of its ions at unit activity. The inclusion of a constant error, however, does not affect the practical utility of these values.

The Significance of Solution Pressure—In spite of the uncertainty just considered it is now generally accepted that the hypothetical 'solution pressure' of a metal is closely connected with its thermionic work function. Taking the absolute potential of the 'normal' calomel electrode as $+0.56$, Lehfeldt* calculated the solution pressures of a number of metals by means of the Nernst equation; the values for zinc, nickel and palladium were 9.9×10^{18} , 1.3 and 1.5×10^{-36} atm. respectively. The great difference between the extreme values indicates that solution pressure cannot be a true pressure; it must represent, in pressure units, the equivalent of other forces operative at the electrode. Various attempts† have been made to evaluate these forces, but the problem cannot be completely solved until the exact mechanism of the ionization of a metal in contact with a solution of its ions—and the reverse process—is known. The following imaginary process involves terms which are within the possibility of measurement or calculation: (i) the metal is vaporized from the electrode; (ii) the vapour is ionized, i.e. dissociated into ions and electrons; (iii) the electrons are returned to the metal, giving it a negative charge; and (iv) the gaseous ions are solvated, and are then assumed to be identical with ions in solution.



* *Phil. Mag.*, 1899, 48, 430.

† Herzfeld, *Ann. Physik*, 1918, 56, 133; Reichinstein, *Z. physikal. Chem.*, 1920, 95, 457; Heyrovský, *Proc. Roy. Soc.*, 1923, 102 A, 628; 1926, 111 A, 201; *J. Physical Chem.*, 1925, 29, 344, 406; *Rec. trav. chim.*, 1925, 44, 447; *Compt. rend.*, 1925, 180, 1655; Butler, *Proc. Roy. Soc.*, 1923, 104 A, 667; *Phil. Mag.*, 1924, 48, 927; *Trans. Faraday Soc.*, 1924, 19, 729; *Chem. and Ind.*, 1926, 45, 3; Rideal, *loc. cit.*; Isgarischev, *Z. Elektrochem.*, 1926, 32, 281; 1928, 34, 128; Hippel, *Z. Physik*, 1927, 45, 471; Hutchisson and Robinson (A. L.), *Physical Rev.*, 1933, 44, 323; Makishima, *Z. Elektrochem.*, 1935, 41, 697; Lange (E.) and Nagel, *ibid.*, 1936, 42, 50; Gross (P.) and Halpern, *J. Chem. Physics*, 1935, 3, 458; Uhara, *Phil. Mag.*, 1936, 21, 958; see also Taylor (H. S.), *Trans. Amer. Electrochem. Soc.*, 1923, 43, 31; Smits, *Theory of Allotropy*, Chap. VII.

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The solution pressure of a metal, which is a measure of its tendency to enter solutions as ions, or of the free energy of the process

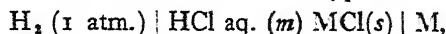
Metal \rightarrow Ions in Solution,

is thus related to the free energy changes concerned in the four stages of the imaginary ionization process. The various free energy terms are (i) vaporization, related to the vapour pressure of the metal ; (ii) ionization, dependent on the ionization potential ; (iii) return of electrons to metal, proportional to the thermionic work function ; and (iv) solvation of gaseous ions. The hypothetical solution pressure can thus be given a significance in terms of definite physical quantities. The standard electrode potential of a metal is related to the solution pressure, and hence it may depend, at least, on the vapour pressure of the metal, its ionization potential, its thermionic work function, and the free energy of solvation of the ions. Hitherto attempts made to calculate electrode potentials have not met with great success as the terms involved are not known with any accuracy, but progress is being made towards elucidation of the problem of solution pressure.

CHAPTER XV

APPLICATIONS OF *E.M.F.* MEASUREMENTS

DETERMINATION of Activities from *E.M.F.* Measurements—If two cells of the type



where M is mercury or silver, in which the acid molalities are m and m' , and the *E.M.F.*'s E and E' respectively, are combined a concentration cell without transport

$\text{H}_2(1 \text{ atm.}) | \text{HCl aq. } (m') \text{ MCl}(s) | \text{M} | \text{MCl}(s) \text{HCl aq. } (m) | \text{H}_2(1 \text{ atm.})$ results. The *E.M.F.* of this cell is $E' - E$, and in it 1 gm. mol. of hydrochloric acid is transferred from the solution of molality m' to that of molality m , during the passage of 1 faraday. The free energy change involved may therefore be written as $(E' - E)F$, or $2RT \ln a_{\pm}'/a_{\pm}$, where a_{\pm}' and a_{\pm} are the mean activities of the acid in the two solutions (p. 305). Hence

$$E' - E = \frac{2RT}{F} \ln \frac{a_{\pm}'}{a_{\pm}} \quad (\text{i})$$

If in one of the two solutions the mean activity a_{\pm}' is equal to unity, and the corresponding *E.M.F.* of the half-cell is E_0 , then

$$E_0 - E = -\frac{2RT}{F} \ln a_{\pm} \quad \dots \quad (\text{ii})$$

At 25°, this may be written

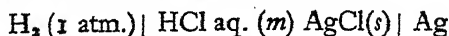
$$E_0 - E = -0.1183 \log a_{\pm} \quad \dots \quad (\text{iii})$$

Adding $0.1183 \log m$ to both sides of this equation there results:

$$\begin{aligned} E_0 - (E - 0.1183 \log m) &= -0.1183 \log \frac{a_{\pm}}{m} \\ &= -0.1183 \log \gamma \quad \dots \quad (\text{iv}) \end{aligned}$$

In order to evaluate E_0 use is made of the fact that at infinite dilution ($m = 0$), the mean activity coefficient γ is equal to unity, and so E_0 will be equal to $E - 0.1183 \log m$. If this expression ($E - 0.1183 \log m$) is plotted as ordinate against a function of the concentration, generally \sqrt{m} , as abscissa, and the curve extrapolated to $m = 0$, then the limiting value of the ordinate is equal

to E_0 . This extrapolation involves a knowledge of the $E.M.F.$'s of cells containing very dilute solutions of hydrochloric acid, and measurements under such conditions are not always accurate. Using the results of Linhart* on the cell



Lewis and Randall† obtained a value for E_0 of -0.2234 volt at 25° ; the difficulty of measurement and of extrapolation to infinite dilution made the result uncertain. As a consequence of a more recent examination of various aspects of the problem it appears that -0.2222 volt at 25° is a more accurate value for E_0 of the hydrogen-silver chloride cell. From measurements of the $E.M.F.$ of similar cells containing finite molalities of hydrochloric acid, the value of γ for various concentrations may be calculated by the use of equation (iv). Some of the results obtained, taken from the work of Randall and Young,‡ are given in Table LII.

TABLE LII

ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID SOLUTIONS (RANDALL AND YOUNG, 1928)

m	0.001	0.005	0.01	0.02	0.05	0.10	0.20	0.50	0.80	1.00
γ	0.965	0.929	0.904	0.874	0.831	0.796	0.767	0.757	0.783	0.810

An alternative method for determining E_0 has been devised by Hitchcock,§ making use of the fact that the activity coefficient of a uni-univalent electrolyte may be expressed in the form

$$-\log \gamma = 0.5\sqrt{m} - Bm \quad . \quad . \quad . \quad (v)$$

(see p. 143). Combining this with equation (iv) there is obtained the relation:

$$E - 0.1183 \log m + 0.0591\sqrt{m} = E_0 + 0.1183Bm \quad . \quad (vi)$$

$$\text{or} \quad E_0' + 0.0591\sqrt{m} = E_0 + 0.1183Bm \quad . \quad (vii)$$

where $E_0' = E - 0.1183 \log m$. At infinite dilution $E - 0.1183 \log m$ is equal to E_0 (*vide supra*), hence $E_0' = E_0$ when m is zero; the value of E_0' at infinite dilution will then be the same as the quantity E_0 required for the determination of activity coefficients. According to equation (vii), $E_0' + 0.0591\sqrt{m}$ should be a linear function of m ; hence by plotting the values of $E - 0.1183 \log m + 0.0591\sqrt{m}$ against m , and extrapolating to $m = 0$ as a

* *J. Amer. Chem. Soc.*, 1919, 41, 1175.

† *Ibid.*, 1921, 43, 1112.

‡ *Ibid.*, 1928, 50, 989; see also Scatchard, *ibid.*, 1925, 47, 641, 2098; Nonhebel, *Phil. Mag.*, 1926, 2, 1085; Roberts (E. J.), *J. Amer. Chem. Soc.*, 1930, 52, 3877; Carmody, *ibid.*, 1932, 54, 188; Wynne-Jones, *ibid.*, p. 2130.

§ *Ibid.*, 1928, 50, 2076; the method has been used by Harned *et al.*, *ibid.*, 1932, 54, 1350; 1933, 55, 2179; 1936, 58, 989.

straight line, the limiting value of the ordinate should be equal to E_0 . Since straight line extrapolation is more reliable than any other type, the results should be more accurate. In practice Hitchcock found that the simple equation was not obeyed exactly, and so the values of $E - 0.1183 \log m + 0.0591 \sqrt{m}$ were plotted for m equal to 0.01, 0.02, 0.05 and 0.1, and the results extrapolated to zero by means of a spline. At 25° , E_0 was evaluated as -0.2223 volt by this method.

By working with amalgam cells of the type

$\text{Ag} | \text{AgCl}(s) \text{ MCl aq. } (m') | \text{MHg}_x | \text{MCl aq. } (m) \text{ AgCl}(s) | \text{Ag}$,
in the form of the half-cells containing MCl at different concentrations, where M is an alkali metal, the activity coefficients of alkali chlorides may be determined; * and for the study of alkali hydroxides the cells

$\text{Hg} | \text{HgO}(s) \text{ MOH aq. } (m') | \text{MHg}_x | \text{MOH aq. } (m) \text{ HgO}(s) | \text{Hg}$
and $\text{H}_2 | \text{MOH aq. } (m') | \text{MHg}_x | \text{MOH aq. } (m) | \text{H}_2$

may be used.† When highly accurate values of the *E.M.F.*'s of the half-cells are not available the extrapolations described cannot be applied with any certainty, and a comparison method must therefore be used. The *E.M.F.* of the complete cell, as already shown (equation i), is given by the expression

$$E = \frac{2RT}{F} \ln \frac{a_{\pm}'}{a_{\pm}} = \frac{2RT}{F} \ln \frac{m'\gamma'}{m\gamma} \quad (\text{viii})$$

If γ is known for any given value of m , then it may be calculated for other values from *E.M.F.* measurements. The activity coefficient at a given concentration may be determined from freezing-point measurements, or by assuming that in very dilute solutions (e.g. < 0.001 molar) the activity coefficient is equal to the conductance ratio. Alternatively it may be assumed that in dilute solution two electrolytes of the same valency type, and similar in other respects, have the same activity coefficient at the same concentration. Another method is to compute the activity of the electrolyte at a given molality by means of the extended form of the Debye-Hückel equation (p. 143), the constants B and C being obtained from the actual *E.M.F.* data.‡ Values for the activity coefficients of alkali halides and hydroxides, and of sulphuric acid are given in Table LIII.

* Allmand and Polack, *J. Chem. Soc.*, 1919, 115, 1020; Harned *et al.*, *J. Amer. Chem. Soc.*, 1929, 51, 416; 1930, 52, 3886; 1932, 54, 423; Smith (R. P.), *ibid.*, 1933, 55, 3279; Gelbach, *ibid.*, p. 4857.

† Knobel, *ibid.*, 1923, 45, 70; Harned *et al.*, *ibid.*, 1925, 47, 676; 1930, 52, 3886; 1932, 54, 1439; 1933, 55, 4838.

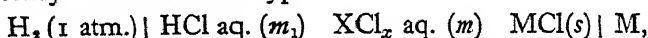
‡ *Idem.*, *ibid.*, 1926, 48, 3226; *loc. cit.*, 1930, 1932.

TABLE LIII
ACTIVITY COEFFICIENTS FROM *E.M.F.* MEASUREMENTS (25°)

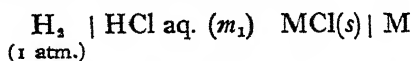
LiCl.	NaCl.	KCl.	KBr.	KI.	H ₂ SO ₄ .	NaOH.	KOH.
0.001	0.966	0.965					0.989
0.005	0.928	0.926					0.954
0.01	0.901	0.903	0.899		0.617	0.902	0.920
0.05	0.819	0.821	0.815	0.816	0.397	0.825	0.822
0.1	0.779	0.778	0.764	0.765	0.313	0.775	0.789
0.5	0.725	0.678	0.644	0.653	0.178	0.702	0.750
1.0	0.757	0.658	0.597	0.612	0.150	0.680	0.760
2.0	0.919	0.670	0.569	0.589	0.646	0.743	
3.0	1.174	0.714	0.571	0.590	0.166	0.838	1.062

In general, activities of any electrolyte may be determined if it is possible to set up a cell with electrodes reversible with respect to *both* ions, so that by combining two such cells a concentration cell without transport is obtained. Provided transport number data are available it is also possible to calculate activity coefficients from measurements on concentration cells with transport.*

Activity Coefficients in Mixtures—The activity coefficients of hydrochloric acid in solutions of chlorides may be determined by a study of cells of the type



where XCl_x is a soluble chloride and M is mercury or silver. If this cell is combined with the element



a cell is obtained, without liquid junction, in which the passage of 1 faraday results in the transfer of 1 gm. mol. of hydrochloric acid from the solution containing the chloride to that of the pure acid. If the *E.M.F.* of the combined cell is E , then

$$E = \frac{RT}{F} \ln \frac{a_{\text{H}^+(\text{S})} \cdot a_{\text{Cl}^-(m+m_1)}}{a_{\text{H}^+(m_1)} \cdot a_{\text{Cl}^-(m_1)}} \quad (\text{ix})$$

where $a_{\text{H}^+(\text{S})}$ is the activity of hydrogen ions in the salt solution. The activity product of hydrochloric acid alone, i.e. $a_{\text{H}^+(m_1)} \times a_{\text{Cl}^-(m_1)}$, at the molality m_1 , may be determined as already described; hence the product in the salt solution may be evaluated from a knowledge of E . The activity coefficient of the acid is then given by the expression

$$\gamma = \left\{ \frac{a_{\text{H}^+(\text{S})}}{m_1} \times \frac{a_{\text{Cl}^-(m+m_1)}}{m+m_1} \right\}^{\frac{1}{2}} \quad \dots \quad (\text{x})$$

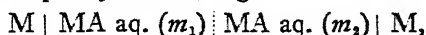
* MacInnes *et al.*, *ibid.*, 1935, 57, 1356; 1936, 58, 1970; *Chem. Reviews*, 1936, 18, 335.

By employing cells of a similar type it has been found possible to determine the activity coefficients of alkali hydroxides in alkali halide solutions, sulphuric acid in sulphate solutions, and halogen acids in halide solutions.* In Table LIV are given some of the results obtained by Harned and his co-workers for hydrochloric acid.

TABLE LIV
ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID (0.1 MOLAL) IN ALKALI CHLORIDE SOLUTIONS

Total Ionic Strength.	HCl alone.	Added :		
		LiCl.	NaCl.	KCl.
0.1	0.824	0.824	0.824	0.824
0.2	0.795	0.798	0.797	0.795
0.3	0.781	0.782	0.774	0.772
0.5	0.775	0.794	0.763	0.754
1.0	0.817	0.846	0.788	0.760
2.0	1.016	1.093	0.950	0.847
3.0	1.343	1.489	1.195	0.978

Individual Ion Activities—The *E.M.F.* of a concentration cell involving a liquid junction, e.g.



may be written in the form

$$E = \frac{RT}{nF} \ln \frac{(a_+)_1}{(a_+)_2} + \pi_d,$$

where π_d is the liquid junction potential. If the latter could be eliminated with certainty, the individual activities of the reversible ions could be compared,† and the actual values determined by extrapolating one of the concentrations to infinite dilution, when $m = a_+$. The splitting up of the *E.M.F.* of the cell indicated above into metal-liquid and liquid-liquid is a purely arbitrary consequence of the application of Nernst's view (p. 299), but it is doubtful whether this division has any real thermodynamic sig-

* For references, see Taylor, *Physical Chemistry*, Vol. I, 1931, p. 801 (Harned), and summaries by Harned, *Trans. Faraday Soc.*, 1927, 23, 462; *Trans. Amer. Electrochem. Soc.*, 1927, 51, 571; also, Loomis, Essex and Meacham, *J. Amer. Chem. Soc.*, 1917, 39, 1113; Ming Chow, *ibid.*, 1920, 42, 488; Harned and Mason, *ibid.*, 1931, 53, 3377; Hawkins, *ibid.*, 1932, 54, 4480; Bates and Urmston, *ibid.*, 1933, 55, 4068; Murdoch and Barton, *ibid.*, p. 4074; and series of papers by Harned *et al.*, cited on p. 213 *supra*.

† See Hass and Jellinek, *Z. physikal. Chem.*, 1932, 162, 153; and criticism, by Náray-Szabó and Szabó, *ibid.*, 1935, 173, 103.

nificance.* The so-called individual ionic activity obtained by the method just described is actually a quantity cf_z , where f_z is an activity coefficient which is really a complicated function depending on the transport numbers of all the ions present *including* those contained in the salt, e.g. potassium chloride, used to 'eliminate' the liquid junction potential.† It is possible that by a suitable combination of circumstances f_z may become virtually equal numerically to the individual activity coefficient of the ions, but thermodynamically it cannot be the *same* quantity.

If the value of π_d could be calculated from the theoretical equation (p. 300), the relative individual ionic activities might be evaluated from measurements of *E.M.F.*; it is evident, however, that the magnitude of π_d itself depends on individual ion activities,‡ and so this method cannot be used. It is generally agreed that although individual ion activities have a thermodynamic significance, it is doubtful if they have any real physical meaning, as far as measurements are concerned.§ For practical purposes, however, the values obtained by 'eliminating' the liquid junction potential, e.g. with the aid of saturated potassium chloride solution, may be regarded as approximate ionic activities in the few cases in which they may be required.

Solubility (Activity) Product of Sparingly Soluble Electrolytes—If MA is a sparingly soluble salt or oxide of the metal M, an electrode of the type: M | MA (solid) NaA aq., where NaA is a soluble substance, is set up and its potential π measured by combining it with a suitable standard electrode; allowance is made for the liquid junction potential, if it cannot be avoided or eliminated. Taking a_M as the activity of the M ions in the saturated solution of MA in NaA aq., and π_0 as the standard electrode potential of M, then

$$\pi = \pi_0 + RT/nF \ln a_M; \dots \dots \dots (xi)$$

if π_0 is known and π measured, a_M may be determined with the limitations mentioned above. Alternatively a cell of the type M | MA(s) NaA aq. || MX aq. | M may be used, where MX is a soluble salt of the metal M at a known concentration (or, better, activity). In order to determine the activity product of MA it is necessary to know the activity of A' in the solution of NaA; if the latter happens to be a chloride, hydroxide, sulphate, or other com-

* Taylor (P. B.), *J. Physical Chem.*, 1927, 31, 1478; Guggenheim, *ibid.*, 1930, 34, 1758.

† Guggenheim, *loc. cit.*

‡ Lewis and Randall, *J. Amer. Chem. Soc.*, 1921, 43, 1112; Harned, *J. Physical Chem.*, 1926, 30, 433; Taylor (P. B.), *loc. cit.*

§ Guggenheim, *loc. cit.*; *ibid.*, 1929, 33, 842; 1930, 34, 1540; *Phil. Mag.*, 1936, 22, 983.

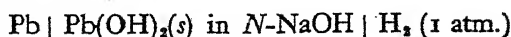
mon salt, the value for the mean activity of the ions can generally be found from published data. The activity of the A' ions may be taken as equal to the mean activity, although this is probably not strictly correct. If activity data for the salt are not available then those for a compound of similar type may be used. As the activity concept has only obtained general acceptance in recent years, the 'concentration' of the A' ions, αc , where α is the 'conductance ratio' and c the concentration of NaA , has been used instead of the activity. For the cell $Ag | AgCl(s) | 0.1N-KCl || 0.1N-AgNO_3 | Ag$, Goodwin found an *E.M.F.* of 0.450 volt at 25° . The conductance ratio for 0.1N-silver nitrate is 0.82, hence the 'concentration' of silver ions in this solution was assumed to be 0.082 gm. ions per litre; applying the simple concentration cell formula, exclusive of diffusion potential, the silver ion 'concentration' in the potassium chloride was found to be 2.24×10^{-9} at 25° . In the latter solution the chlorine ion 'concentration', calculated from the conductance ratio, is 0.085 gm. ions per litre; hence the solubility product $[Ag^+][Cl^-]$ is 1.91×10^{-10} at 25° . If the silver chloride is assumed to be completely ionized into silver and chlorine ions, then the solubility, s , in pure water is given by

$$s = \sqrt{[Ag^+][Cl^-]} = 1.38 \times 10^{-5} \text{ gm. mol. per litre at } 25^\circ.$$

The activity solubility product of silver chloride could have been determined from measurements on the cell $Ag | KCl \text{ solution saturated with } AgCl | Cl_2$; the *E.M.F.* is expressed by

$$\begin{aligned} E &= \frac{\pi_0}{Ag, Ag'} + \frac{RT}{F} \ln a_{Ag} - \frac{\pi_0}{Cl, Cl'} + \frac{RT}{F} \ln a_{Cl'} \\ &= \frac{\pi_0}{Ag, Ag'} - \frac{\pi_0}{Cl, Cl'} + \frac{RT}{F} \ln (a_{Ag} \times a_{Cl'}) \end{aligned} \quad (xii)$$

Since π_0 and π_0 are the known standard potentials, the activity product ($a_{Ag} \times a_{Cl'}$) can be determined from the measurement of the *E.M.F.* of the cell. If the oxygen electrode were reversible the activity product of hydroxides might be obtained in a similar manner, but a hydrogen electrode may be used instead; thus for lead hydroxide the cell



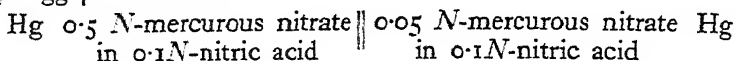
has an *E.M.F.*,

$$\begin{aligned} E &= \frac{\pi_0}{Pb, Pb^{2+}} + \frac{RT}{2F} \ln a_{Pb^{2+}} - \frac{\pi_0}{H, H^+} - \frac{RT}{F} \ln a_{H^+} \\ &= \frac{\pi_0}{Pb, Pb^{2+}} - \frac{\pi_0}{H, H^+} - \frac{RT}{F} \ln K_w + \frac{RT}{2F} \ln (a_{Pb^{2+}} \times a_{OH^{2-}}) \end{aligned} \quad (xiii)$$

since K_w may be used instead of $a_{H^+} \times a_{OH^-}$. At 25° , E is 0.252 volt, π_0 is -0.120 , π_0 is ± 0 and K_w equals 1.0×10^{-14} ,
 Pb, Pb^{++} H, H^+

hence the activity solubility product of lead hydroxide is 4.0×10^{-16} . It is not necessary, of course, actually to set up this cell, as its *E.M.F.* may be calculated from measurements of the two separate electrodes against suitable standards.*

Valency of Ions—The application of electrode potentials to the determination of the valency of the mercurous ion was made by Ogg.† The cell



was set up, and the *E.M.F.* (E) measured. If a_1 and a_2 are the mercurous ion activities in the two solutions,

$$E = \frac{RT}{nF} \ln \frac{a_1}{a_2} = \frac{0.058}{n} \log \frac{a_1}{a_2} \text{ at } 17^\circ \quad (\text{xiv})$$

the diffusion potential being negligible. In the cell used a_1/a_2 is approximately 10, the ratio of the concentrations, and E was found to be 0.029 volt at 17° ; hence n is equal to 2. The mercurous ion is, therefore, bivalent and must be written Hg_2^{++} ; the nitrate is $Hg_2(NO_3)_2$ and the chloride Hg_2Cl_2 . This method has also been used to determine the valency of tellurium in potassium telluride and in tellurium chloride.‡

Transport (or Transference) Numbers—The method was originally suggested by Helmholtz,§ but owing to difficulties in setting up and measuring the *E.M.F.*'s of the cells involved it was not used to any extent until recently. The *E.M.F.* of a concentration cell *with transport* (p. 292) may be written :

$$E_t = n \frac{v}{v_r} \frac{RT}{nF} \ln \frac{a_1}{a_2}, \quad (\text{xv})$$

* For examples of the use of *E.M.F.* methods to determine solubility products, see Goodwin, *Z. physikal. Chem.*, 1894, **13**, 577; Abegg and Cox, *ibid.*, 1903, **46**, 1; Spencer and Le Pla, *Z. anorg. Chem.*, 1909, **65**, 10; Spencer, *Z. physikal. Chem.*, 1912, **80**, 701; Allmand, *Z. Elektrochem.*, 1910, **16**, 254; *J. Chem. Soc.*, 1909, **95**, 2151; Glasstone, *ibid.*, 1921, **119**, 1914; Buckley and Hartley, *Phil. Mag.*, 1929, **8**, 320; Johnson and Low, *J. Physical Chem.*, 1932, **36**, 2390; *J. Amer. Chem. Soc.*, 1933, **55**, 2262; Brown (A. S.) and MacInnes, *ibid.*, 1935, **57**, 459; Hass and Jellinek, *loc. cit.* See also, Walden-Drucker, *Handbuch der allgemeinen Chemie*, Vol. VIII, Part I, 1930, p. 129 (Kremann and R. Müller).

† *Z. physikal. Chem.*, 1898, **27**, 285.

‡ Reichinstein, *ibid.*, 1921, **97**, 257; Kasarnowsky, *Z. anorg. Chem.*, 1923, **128**, 17.

§ *Ges. Abh.*, I, 840, II, 979; for early applications see McIntosh, *J. Physical Chem.*, 1898, **2**, 273; Kendrick, *Z. Elektrochem.*, 1900, **7**, 52; Gans, *Ann. Physik*, 1901, **6**, 315.

where n_i is the transport number of the ion for which the cell is not reversible, and ν_r refers to the other ion. For the same cell *without transport*

$$E = \frac{\nu_r RT}{\nu_r nF} \ln \frac{a_1}{a_2}, \quad . \quad . \quad . \quad (xvi)$$

hence
$$\frac{E_t}{E} = n_i \quad (xvii)$$

The transport number is thus determined by the ratio of the *E.M.F.*'s of the two concentration cells. The weakness of the method is that it gives the mean transport number of the ion over the concentration range involved in the cells examined. Since transport numbers frequently vary with the dilution of the solution, the results are not satisfactory; in such cases the modified procedure suggested by MacInnes and Beattie* may be used. If cells are considered in which the concentrations of the electrolyte are very close, that is to say with mean activities of $a + da$ and a , respectively, the transport number may be taken as constant; it is then possible to write

$$dE_t = n_i \frac{\nu_r RT}{\nu_r nF} d \ln a \quad (xxviii)$$

and
$$dE = \frac{\nu_r RT}{\nu_r nF} d \ln a \quad (xxix)$$

utilizing the fact that $\ln(a + da)/a$ is practically equal to da/a , which is $d \ln a$. From equation (xxviii) and (xxix) it follows that

$$\frac{dE_t}{d \ln a} \bigg/ \frac{dE}{d \ln a} = \frac{dE_t}{d \log a} \bigg/ \frac{dE}{d \log a} = n_i \quad (xx)$$

If the *E.M.F.*'s of the cells, with and without transport, in which the concentration of one of the solutions is varied and of the other kept at a constant low value, e.g. 0.001 mol./litre, are plotted against $\log a$ of the variable solution, the slopes of the curves are $dE_t/d \log a$ and $dE/d \log a$ respectively.† The transport number of the 'non-reversible' ion may thus be determined at any concentration, from the ratio of the slopes at the value of a corresponding to this concentration.

In view of the difficulty in measuring precisely the slope of the curves, MacInnes and Beattie used a mathematical method: E_t was expressed as an empirical function of the activity, thus:

$$E_t = x + y \log a + z (\log a)^2,$$

* *J. Amer. Chem. Soc.*, 1920, 42, 1117.

† The value of a may be obtained from *E.M.F.* or other measurements.

appropriate values of x , y and z being found to fit the experimental results. Differentiating with respect to $\log a$,

$$dE_t/d \log a = y + z \log a \quad \text{. (xxi)}$$

For a uni-univalent electrolyte v/v_r is 2, and n equals 1 hence from equation (xix)

$$dE/d \log a = 2 \cdot 302 \frac{v}{v_r} \frac{RT}{nF} = 0 \cdot 1183 \text{ at } 25^\circ \quad \text{(xxii)}$$

$$\text{Therefore, } n_t = \frac{dE_t}{d \log a} \bigg/ \frac{dE}{d \log a} = \frac{y + z \log a}{0 \cdot 1183} \quad \text{(xxiii)}$$

For the cells $\text{Ag} | \text{AgCl}(s) | \text{LiCl aq. } (c_1) | \text{LiCl aq. } (c_2) | \text{AgCl}(s) | \text{Ag}$, it was found that

$$E_t = -43 \cdot 865 + 45 \cdot 363 \log A - 1 \cdot 4902 (\log A)^2$$

where $A = a \times 10^4$, and so

$$n_{\text{Li}} = 0 \cdot 3834 - 0 \cdot 02529 \log A.$$

By making use of the fact that the activity coefficient can be expressed as a function of the concentration, and two empirical constants, by means of the extended form of the Debye-Hückel equation, it has been shown by G. Jones and Dole * that a more rigid, although more laborious, method is available for calculating transport numbers from the *E.M.F.* measurements. Using the data of MacInnes and Beattie, the variation of transport number of the lithium ion with the concentration of lithium chloride can be expressed by the relationship

$$n_{\text{Li}} = [1 \cdot 3394 / (1 + 0 \cdot 04565 \sqrt{c})] - 1,$$

as compared with the corresponding expression for the results obtained by the Hittorf method,†

$$n_{\text{Li}} = [1 \cdot 3337 / (1 + 0 \cdot 03605 \sqrt{c})] - 1.$$

Some of the values of the transport number given by these equations have been calculated at a number of rounded concentrations and are quoted in Table LV: the differences are not very large and are probably due to experimental errors in one or both sets of measurements.

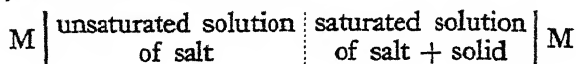
The *E.M.F.* method for determining transport numbers has been used frequently in recent years, since concentration cells without transport have become more common.‡

* *Ibid.*, 1929, 51, 1073; see also, Jones (G.) and Bradshaw, *ibid.*, 1932, 54, 138.

† Jones and Bradshaw, *loc. cit.*

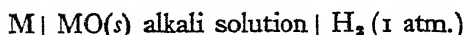
‡ MacInnes and Parker (H. C.), *J. Amer. Chem. Soc.*, 1915, 37, 1445; Ferguson, *J. Physical Chem.*, 1916, 20, 326; Pearce and Mortimer, *J. Amer. Chem. Soc.*, 1918, 40, 509; Beattie, *ibid.*, 1920, 42, 1128; Pearce and Hart, *ibid.*, 1921, 43, 2483; Knobel *et al.*, *ibid.*, 1923, 45, 70, 77;

In another method the use of the metastable phase is not involved; * the concentration cell



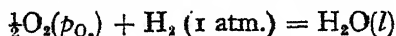
is set up and its *E.M.F.* determined at various temperatures. The concentration of the unsaturated solution is kept constant, and so the *E.M.F.* depends on the concentration of the saturated solution; the *E.M.F.*-temperature curve should be similar to the solubility-temperature curve. The latter always shows a 'break' at the transition point, and so also will the former.†

Dissociation Pressures of Oxides—The reaction occurring in the cell

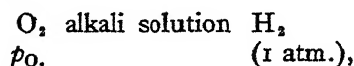


is $MO(s) + H_2 (1 \text{ atm.}) = H_2O(l) + M.$

The free energy is the same as for the reaction



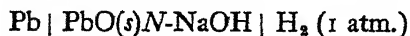
occurring in the cell



where p_{O_2} , the pressure of the oxygen, is equal to the equilibrium dissociation pressure of the oxide MO at the temperature of the experiment.‡ Hence the first cell may be regarded as an oxygen-hydrogen cell with oxygen at the dissociation pressure of the oxide MO . The *E.M.F.* of any oxygen-hydrogen cell is given by the equation

$$E = k + \frac{RT}{2F} \ln p_H + \frac{RT}{4F} \ln p_{O_2} \quad \dots \quad (xxiv)$$

where k is a constant, and p_H and p_{O_2} are the pressures of the two gases. The constant k is equal to the *E.M.F.* of the cell when both gases are at atmospheric pressure, i.e. 1.226 volt at 25° (p. 335); hence if E is measured p_{O_2} may be calculated. For the cell



E is 0.247 volt at 25°; hence

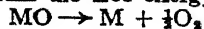
$$0.247 = 1.226 + \frac{0.059}{4} \log p_{O_2}$$

$$\therefore p_{O_2} = 4.2 \times 10^{-87} \text{ atm. at } 25^\circ.$$

* Cohen and Bredig, *Z. physikal. Chem.*, 1894, 14, 535.

† Mason and Matthews, *J. Physical Chem.*, 1925, 29, 1507; Cohen and Joss, *J. Amer. Chem. Soc.*, 1928, 50, 727.

‡ Note that at equilibrium the free energy of the reaction



is zero.

In the application of this method it is not necessary to measure the *E.M.F.* of the actual cell described, but the value may be determined from separate measurements on the two individual electrodes. Thus the potential of the half-elements $M | MO(s)$ in alkali, and $H_2(1 \text{ atm.}) | \text{alkali}$ may both be measured against a standard calomel electrode and the results combined.*

By means of the integrated form of the van 't Hoff isochore it is possible to determine the dissociation pressures at other temperatures, provided the heat of dissociation is known, and may be regarded as constant. When the dissociation pressure of an oxide is 0.21 atm., that is equal to the partial pressure of oxygen in air, the oxide will decompose completely if heated in air; the temperature at which this occurs may be calculated by the use of the isochore from a knowledge of the dissociation pressure at one temperature.†

The dissociation pressures of chlorides, and of higher to lower oxides may be determined from *E.M.F.* measurements in a similar manner to that described for simple oxides.‡

Hydrogen Ion Activities—The potential of a hydrogen electrode at a definite pressure is given by the general formula

$$\pi = \frac{\pi_0}{H, H} + \frac{RT}{F} \ln a_H. \quad (\text{xxv})$$

where $\frac{\pi_0}{H, H}$ is the standard electrode potential for the given pressure, and a_H is the hydrogen ion activity of the solution. If the pressure is 760 mm. of mercury § and the potentials are measured on the 'hydrogen scale', $\frac{\pi_0}{H, H}$ is zero, and

$$\pi = \frac{RT}{F} \ln a_H. \quad (\text{xxvi})$$

* For applications, see Rothmund, *Z. physikal. Chem.*, 1899, **31**, 69; Lewis, *ibid.*, 1906, **55**, 449; Allmand, *Z. Elektrochem.*, 1910, **16**, 254; *J. Chem. Soc.*, 1909, **95**, 2151; 1910, **97**, 603; Glasstone, *ibid.*, 1921, **119**, 1914.

† If the dissociation pressure of an oxide is known, with certain other data, the standard electrode potential of the metal may be calculated (Lamb, *J. Amer. Chem. Soc.*, 1910, **32**, 1214).

‡ Sackur and Fritzmann, *Z. Elektrochem.*, 1909, **15**, 842; Glasstone, *J. Chem. Soc.*, 1922, **121**, 1469.

§ As the gas in the ordinary hydrogen electrode has been bubbled through a solution its pressure will be equal to $B - v$, where B is the barometric pressure and v the saturation vapour pressure of the solution. A correction should be made for the deviation of the actual pressure from 760 mm. by means of equation (xliii), p. 310; this correction is generally negligible except for accurate work (see Britton, *Hydrogen Ions*, 1932, p. 53).

If π can be measured, therefore, by combining the hydrogen electrode with a standard electrode of known potential and measuring the *E.M.F.* by means of a potentiometer, a quantity equal to a_{H} may be determined, provided the liquid junction potential is completely eliminated (see p. 367). This limitation applies to all measurements of so-called individual hydrogen ion activities, and as an approximation they are often termed 'hydrogen ion concentrations', although they are not identical with the true concentrations which may be determined by special methods.*

The hydrogen electrode is generally prepared by coating a piece of smooth platinum foil or wire with platinum black by the electrolysis of a 2 per cent. solution of platinic chloride. There has been some doubt as to the advisability of adding lead acetate to the platinizing solution,† but it seems to be generally accepted that the addition of 0.02 gm. of this salt to 100 c.c. of solution gives a deposit suitable for use as a hydrogen electrode.‡ The efficiency of these electrodes varies with the physical nature of the platinum black, but in spite of the considerable work done with the hydrogen electrode it does not yet seem possible to lay down the exact conditions under which satisfactory results may be obtained. Other metals have been employed for gas electrodes, e.g. gold coated with palladium black,§ iridium coated on glass or on gold.||

Electrode vessels of various types have been devised for different solutions; ** one of the simplest and most generally useful is that due to Hildebrand.†† A rectangular piece of platinum foil (1 to 3 sq. cm.), subsequently platinized, is welded to a short length of wire sealed into a glass tube containing mercury. This tube is enclosed in another, closed at the top but open and widened at the bottom surrounding the foil (Fig. 25); a side connection is provided for the inlet of hydrogen. A number of holes are made in the wide part of the tube at a level mid-way up the platinum foil, so that when the electrode is inserted in a solution and hydro-

* See references on p. 200 *supra*.

† Ellis, *J. Amer. Chem. Soc.*, 1916, 38, 737.

‡ Britton, *J. Chem. Soc.*, 1924, 125, 1573; Cady, Kemmerer and Week, *J. Physical Chem.*, 1929, 33, 1770. Excessive platinizing must be avoided, cf. Thiel and Coch, *Z. anorg. Chem.*, 1932, 208, 397.

§ Böttger, *Z. physikal. Chem.*, 1897, 24, 251; Treadwell and Weiss, *Helv. Chim. Acta*, 1920, 2, 433.

|| Westhaver, *Z. physikal. Chem.*, 1905, 51, 90; Lewis, Brighton and Sebastian, *J. Amer. Chem. Soc.*, 1917, 39, 2245. See also Lorch, *Ind. Eng. Chem. (Anal.)*, 1934, 6, 164.

** Britton, *op. cit.*, p. 55; Clark, *The Determination of Hydrogen Ions*, 1928, p. 290 *et seq.*; Bollen, *Ind. Eng. Chem. (Anal.)*, 1931, 3, 203; Lindsey, *Analyst*, 1932, 57, 573; Lockwood, *J. Soc. Chem. Ind.*, 1935, 54, 295 T.

†† *J. Amer. Chem. Soc.*, 1913, 35, 847; cf. also, Sand *et al.*, *J. Soc. Chem. Ind.*, 1911, 30, 871.

gen passed in through the side-tube the foil is half immersed in liquid and half surrounded by gas; this is usually the best arrangement for obtaining rapid equilibrium and reproducible potentials.* The time taken to reach equilibrium depends, amongst other factors, on the nature of the solution, the thickness of the deposit and on previous use.† As a general rule the hydrogen electrode cannot be used in solutions, containing oxidizing agents, e.g. nitrates, chlorates, permanganates and ferric salts, or other substances capable of reduction, e.g. sulphites, sulphides, sulphur, unsaturated and reducible organic compounds, and alkaloids. It is also readily 'poisoned' by arsenic and other catalytic poisons.‡ The electrode is not satisfactory in solutions of salts of more noble metals, e.g. copper, silver, gold and mercury, since they are replaced by hydrogen; it is also unreliable in the presence of lead, cadmium and thallous salts.§ It has been shown that by taking special precautions the hydrogen electrode may be used in the presence of ferric salts and of chromates.|| The electrode has also been employed in various non-aqueous solvents with fairly satisfactory results, e.g. alcohols, acetone, benzene, liquid ammonia, etc.**

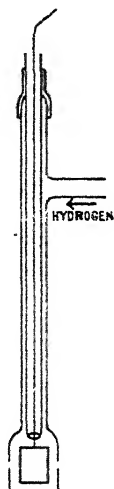


FIG. 25.—
The Hildebrand
hydrogen electrode

* The hydrogen gas should be free from oxygen, carbon dioxide, sulphuretted hydrogen, arsenic compounds and hydrocarbons; for generators and purifiers, see Clark, *op. cit.*

† Aten, *Trans. Amer. Electrochem. Soc.*, 1923, 43, 89; Beans and Hammett, *J. Amer. Chem. Soc.*, 1925, 47, 1215.

‡ Isgarischev and Koldaeva, *Z. Elektrochem.*, 1924, 30, 83; Aten and Zieren, *Rec. trav. chim.*, 1929, 48, 944; *Trans. Amer. Electrochem. Soc.*, 1930, 58, 109; for methods of avoiding poisoning, see Thiel and Schulz, *Z. Elektrochem.*, 1930, 36, 408; de Nouy, *Compt. rend.*, 1932, 195, 1265.

§ Denham and Allmand, *J. Chem. Soc.*, 1908, 93, 424; Denham, *ibid.*, p. 833; Denham and Marris, *Trans. Faraday Soc.*, 1928, 24, 510; see also Kolthoff and Kameda, *J. Amer. Chem. Soc.*, 1929, 51, 2188; 1931, 53, 832; Čupr and Viktorin, *Z. anorg. Chem.*, 1931, 198, 363.

|| Browne, *J. Amer. Chem. Soc.*, 1923, 45, 297; Britton, *J. Chem. Soc.*, 1924, 125, 1572. For technique see Popoff, Kunz and Snow, *J. Physical Chem.*, 1928, 32, 1056; for high temperatures: Kolthoff and Tekelenburg, *Rec. trav. chim.*, 1927, 46, 18; Stone, *ibid.*, 1930, 49, 1133; for a consideration of various errors, see Fletcher and Westwood, *J. Soc. Chem. Ind.*, 1930, 49, 201T; for modified hydrogen electrodes: Knobel, *J. Amer. Chem. Soc.*, 1923, 45, 1723; Schmid, *Helv. Chim. Acta*, 1924, 7, 370; Glasstone, *Analyst*, 1925, 50, 327; Drucker, *Z. Elektrochem.*, 1927, 33, 504; Biilmann and Klit, *Z. physikal. Chem.*, 1927, 130, 566.

** Fredenhagen, *ibid.*, 1928, 134, 41; Shukov and Vorochobin, *J. Gen. Chem. Russia*, 1932, 2, 399; Tomiček and Feldmann, *Coll. Czech. Chem. Comm.*, 1934, 6, 408; Goodhue and Hixon, *J. Amer. Chem. Soc.*, 1935, 57, 1688.

The Oxygen Electrode—If the hydrogen electrode is quite inapplicable other electrodes may be used. Unfortunately the oxygen electrode is not reversible, but in spite of this it has been employed to indicate roughly the hydroxyl, and hence the hydrogen, ion concentration of solutions containing reducible substances. Air, which contains oxygen at a more or less definite partial pressure, has been substituted for pure oxygen. The electrode must be standardized empirically by means of solutions of known hydrogen ion concentration. Platinized platinum is generally used as electrode metal, but platinized gold is said to be better.*

The Quinhydrone Electrode—In a previous section (p. 342) it was found that the oxidation-reduction potential of the system hydroquinone-quinone was represented by the equation

$$\pi = \pi_0 + \frac{RT}{2F} \ln \frac{a_{\text{Quinone}}}{a_{\text{Hydroquinone}}} + \frac{RT}{F} \ln a_{\text{H}}. \quad (\text{xxvii})$$

If the solution always contains equivalent amounts of hydroquinone and quinone, the ratio of the activities may be regarded as constant; this condition is attained by adding quinhydrone, a molecular compound of quinone and hydroquinone, viz. $\text{C}_6\text{H}_4\text{O}_2 \cdot \text{C}_6\text{H}_4(\text{OH})_2$. The equation for the electrode potential then reduces to

$$\pi = \pi_0 + \frac{RT}{F} \ln a_{\text{H}}. \quad (\text{xxviii})$$

and if π is measured and π_0 known a_{H} may be determined.† The limitation concerning the significance of a_{H} , pointed out above, is applicable here also. The value of π_0 is determined by measurements in solutions of known hydrogen ion 'activity'; it has been found to be given, on the hydrogen scale, by the formula

$$\pi_0 = 0.7181 - 0.00074t \quad . \quad . \quad . \quad (\text{xxix})$$

between temperatures (t) of 0° and 37°C .‡ In order to determine the pH , or hydrogen ion 'activity,' of a solution it is shaken with a small amount of pure quinhydrone, a clean polished platinum or

* For details see Furman, *J. Amer. Chem. Soc.*, 1922, 44, 12; *Trans. Amer. Electrochem. Soc.*, 1923, 43, 79; Tilley and Ralston, *ibid.*, 1923, 44, 31; Montillon and Cassel, *ibid.*, 1924, 45, 259; Britton, *J. Chem. Soc.*, 1925, 127, 1896, 2148; Náray-Szabó, *Z. Elektrochem.*, 1927, 33, 15; Richards, *J. Physical Chem.*, 1928, 32, 990; Tartar and Wellman, *ibid.*, p. 1171; Britton, *op. cit.*, p. 78; see also Butler and Armstrong, *Trans. Faraday Soc.*, 1933, 29, 862.

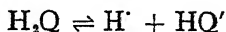
† Büllmann *et al.*, *Ann. Chim. physique*, 1921, 15, 109; 1921, 16, 321; 1923, 19, 137; *Trans. Faraday Soc.*, 1923, 19, 676; *Bull. Soc. Chim.*, 1927, 41, 151, 213.

‡ *Idem.*, *J. Chem. Soc.*, 1924, 125, 1954; *Bull. Soc. Chim.*, 1927, 41, 151; see Clark, *op. cit.*, 1928, p. 419. A more complicated formula of greater accuracy is given by Harned and Wright, *J. Amer. Chem. Soc.*, 1933, 55, 4849.

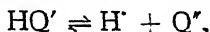
gold electrode is inserted and the potential difference between metal and solution is measured by combination with a standard, e.g. calomel, electrode. Stirring the solution with nitrogen is sometime advantageous.* The potential is converted to the hydrogen scale and from it a_{H} may be determined by application of equation (xxviii).†

The quinhydrone electrode is applicable in the presence of many reducible substances, e.g. dilute nitric acid and nitrates, copper, zinc, lead and cadmium salts, alkaloids and unsaturated acids, but it may be erratic in the presence of ammonium salts.‡ It attains equilibrium very rapidly and is not easily poisoned; on the other hand it is not reliable in solutions of pH greater than 8§ and has appreciable salt and protein errors.|| The salt error is probably connected with the influence on the relative activities of quinone and hydroquinone, the ratio varying from unity.

The erratic behaviour above pH 8 is due to two causes; in the first place oxidation of hydroquinone by air occurs readily in alkaline solution,** and in the second place ionization of hydroquinone as an acid becomes appreciable and affects the electrode potential. Consider the acid ionization of hydroquinone (H_2Q), thus ††



and



$$K_1 = \frac{[\text{H}^+][\text{HQ}']}{[\text{H}_2\text{Q}]} \cdot \frac{f_{\text{H}} \cdot f_{\text{HQ}'}}{f_{\text{H}_2\text{Q}}} \text{ and } K_2 = \frac{[\text{H}^+][\text{Q}']}{[\text{HQ}']} \cdot \frac{f_{\text{H}} \cdot f_{\text{Q}'}}{f_{\text{HQ}'}} \quad (\text{xxx})$$

If S_{H} is the total concentration of hydroquinone in the solution, then

$$S_{\text{H}} = [\text{H}_2\text{Q}] + [\text{HQ}'] + [\text{Q}'] \quad (\text{xxxix})$$

$$= \frac{[\text{H}^+]^2 [\text{Q}']}{K_1 K_2} \cdot \frac{f_{\text{H}}^2 f_{\text{Q}'}}{f_{\text{H}_2\text{Q}}} + \frac{[\text{H}^+][\text{Q}']}{K_2} \cdot \frac{f_{\text{H}} f_{\text{Q}'}}{f_{\text{HQ}'}} + [\text{Q}'] \quad (\text{xxxii})$$

* Morgan *et al.*, *ibid.*, 1931, 53, 454.

† For comprehensive studies of the reproducibility and accuracy of the quinhydrone electrode, see Morgan and Lammert, *ibid.*, 1931, 53, 454, 597, 2154; 1932, 54, 910; *Trans. Amer. Electrochem. Soc.*, 1932, 61, 199 (with Campbell; contains full references).

‡ Shikata and Tachi, *J. Biochem. (Japan)*, 1928, 10, 115.

§ La Mer and Parsons, *J. Biol. Chem.*, 1923, 57, 613. In unbuffered solutions the limit is pH 5 (Best, *J. Physical Chem.*, 1930, 34, 1815).

|| Sørensen, Sørensen and Linderström-Lang, *Ann. Chim. phys.*, 1921, 15, 111; 1921, 16, 283; *Compt. rend. Lab. Carlsberg*, 1921, 14, 1; Linderström-Lang, *ibid.*, 1924, 15, 1; 1925, 16, 1; Kolthoff, *Z. physiol. Chem.*, 1925, 144, 259; Hovorka and Dearing, *J. Amer. Chem. Soc.*, 1935, 57, 446.

** La Mer and Rideal, *ibid.*, 1924, 46, 223.

†† For discussion of theory of quinhydrone electrode, see Brodsky and Trachtenberg, *Z. physikal. Chem.*, 1929, 143, 287.

If $f_{H,Q}$ and $f_{H,Q'}$ may be assumed to be almost equal to unity, then equation (xxxii) may be written in the form

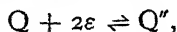
$$S_H = [Q']f_Q \left\{ \frac{[H']^2 f_H^2}{K_1 K_2} + \frac{[H'] f_H}{K_2} + \frac{1}{f_Q'} \right\} \quad \text{. . . (xxxiii)}$$

$$\therefore f_Q [Q'] = \frac{K_1 K_2 S_H}{[H']^2 f_H^2 + [H'] f_H K_1 + f_Q' K_1 K_2} \quad \text{. . . (xxxiv)}$$

Since $K_1 K_2$ is small the value of f_Q' in the term $f_Q' K_1 K_2$ may be put equal to unity; further $f_H [H']$ may be replaced by a_H , hence the equation reduces to

$$f_Q [Q'] = \frac{K_1 K_2 S_H}{a_H^2 + K_1 a_H + K_1 K_2} \quad \text{. . . (xxxv)}$$

For the oxidation-reduction system consisting of quinone (Q) and the anion of hydroquinone (Q)', viz.



the reversible potential would be given by

$$\pi = \pi_0 + \frac{RT}{2F} \ln \frac{a_Q}{a_{Q'}} \quad \text{(xxxvi)}$$

where a_Q and $a_{Q'}$ are the activities of Q and Q' respectively. Since the activity coefficient of the un-ionized quinone may be regarded as unity,

$$\pi = \pi_0 + \frac{RT}{2F} \ln \frac{[Q]}{[Q']f_Q'} \quad \text{. . . (xxxvii)}$$

Substituting the value for $[Q']f_Q'$ given in equation (xxxv), it follows that

$$\begin{aligned} \pi = \pi_0 - \frac{RT}{2F} \ln K_1 K_2 - \frac{RT}{2F} \ln \frac{S_H}{[Q]} \\ + \frac{RT}{2F} \ln (a_H^2 + K_1 a_H + K_1 K_2) \quad \text{. . . (xxxviii)} \end{aligned}$$

Since π_0 , K_1 and K_2 are constants,

$$\pi_0 - \frac{RT}{2F} \ln K_1 K_2 = \text{a constant, } \xi_0$$

$$\therefore \pi = \xi_0 + \frac{RT}{2F} \ln \frac{[Q]}{S_H} + \frac{RT}{2F} \ln (a_H^2 + K_1 a_H + K_1 K_2) \quad \text{(xxxix)}$$

The values of K_1 and K_2 are 1.75×10^{-10} and 4×10^{-12} respectively; * hence as long as a_H is fairly large the terms $K_1 a_H$ and $K_1 K_2$ are negligible in comparison with a_H^2 , and the equation reduces to the normal form

$$\pi = \xi_0 + \frac{RT}{F} \ln a_H \quad \text{. . . (xxviii)}$$

* Sheppard, *Trans. Amer. Electrochem. Soc.*, 1921, 39, 427.

If a_{H^+} is less than about 10^{-8} , that is $p\text{H}$ greater than 8, the value of $K_1 a_{\text{H}^+}$ becomes appreciable in comparison with $c_{\text{H}^+}^2$, and the simple relation is no longer applicable. Differentiating equation (xxxix) with respect to $\ln a_{\text{H}^+}$, it is found that

$$\frac{d\pi}{d \ln a_{\text{H}^+}} = \frac{d\pi}{-dp\text{H}} = \frac{RT}{2F} \frac{2a_{\text{H}^+}^2 + K_1 a_{\text{H}^+}}{a_{\text{H}^+}^2 + a_{\text{H}^+} K_1 + K_1 K_2} \quad (\text{xl})$$

When a_{H^+} is large, the value of the expression to the right of $RT/2F$ reduces to 2, and $d\pi/-dp\text{H}$ is equal to RT/F ; if a_{H^+} is equal to $\sqrt{K_1 K_2}$, the expression becomes unity, and $d\pi/-dp\text{H}$ is $RT/2F$; if a_{H^+} is still smaller the value of $d\pi/-dp\text{H}$ approaches zero. These results mean that although equation (xxviii) applies up to $p\text{H}$ 8 or 9, at larger $p\text{H}$'s it is no longer applicable; at about $p\text{H}$ 10.5 ($a_{\text{H}^+} = \sqrt{K_1 K_2}$) the equation

$$\pi = \xi_0 + \frac{RT}{2F} \ln a_{\text{H}^+} \quad \dots \dots \dots (\text{xli})$$

applies, and at still larger $p\text{H}$'s the electrode potential approaches a constant value (ξ_0). It is clear, therefore, that the quinhydrone electrode does not function as a simple hydrogen electrode at $p\text{H}$'s above 9.

The quinhydrone electrode has been used in heavy water,* as well as in a number of non-aqueous media:† in the latter the platinum electrode is often replaced with advantage by one consisting of gold deposited on glass. For the determination of hydrogen ion activities in acetic acid a modified form of the quinhydrone electrode involving tetrachloroquinone and its hydroquinone has been used: it is generally known as the chloranil electrode.‡

The Glass Electrode—Haber and Klemensiewicz § found that the potential difference between a glass surface and a solution varied regularly with the $p\text{H}$ of the solution; in recent years this observation has been made the basis of a method of measuring the hydrogen ion concentration of solutions in which the hydrogen

* Korman and La Mer, *J. Amer. Chem. Soc.*, 1936, 58, 1396.

† Various alcohols and alcohol-water mixtures (Ebert, *Ber.*, 1925, 58, 175; Biillmann and Katagin, *Biochem. Z.*, 1927, 21, 441; Kuhn and Wassermann, *Helv. Chim. Acta*, 1928, 11, 31, 44, 50; Macfarlane, *J. Chem. Soc.*, 1931, 3212; Halford, *J. Amer. Chem. Soc.*, 1931, 53, 2944; Wooten and Hammett, *ibid.*, 1935, 57, 2289); acetone (Pring, *Trans. Faraday Soc.*, 1923, 19, 705); formic acid (Hammett and Dietz, *J. Amer. Chem. Soc.*, 1930, 52, 4795); benzene (La Mer and Downes, *ibid.*, 1931, 53, 888; 1933, 55, 1840); liquid ammonia (Zintl and Neumayr, *Ber.*, 1930, 63, 337); see also Tomíček and Feldmann, *loc. cit.*, and Shukov and Vorochobin, *loc. cit.*

‡ Conant *et al.*, *J. Amer. Chem. Soc.*, 1925, 47, 1959; 1927, 49, 3047; Heston and Hall (N. F.), *ibid.*, 1934, 56, 1462; also, *idem.*, *ibid.*, 1933, 55, 4729.

§ *Z. physikal. Chem.*, 1909, 67, 385.

or quinhydrone electrode cannot be used. The experimental arrangement is shown diagrammatically in Fig. 26; the glass bulb *A* is thin walled (0.001 mm. if possible) and preferably made of low melting-point glass of high electrical conductivity.* This bulb contains an electrode which has a constant potential, e.g. silver coated with silver chloride dipping into hydrochloric acid solution, or a platinum wire inserted in a buffer solution containing a little quinhydrone. In the beaker (*B*) is placed the solution being tested for its hydrogen ion concentration, and into this dips the tip of a calomel, or other reference, electrode. The wire constituting the electrode in *A* and the reference electrode are connected to the potentiometer for measurement of the *E.M.F.* In view of the very high resistance, viz., 10 to 100 megohms or

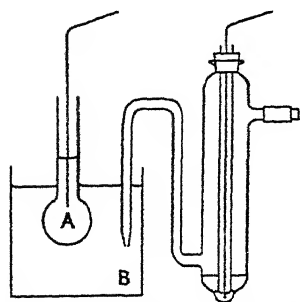


FIG. 26.—The glass electrode

more, of the glass electrode special methods have to be used to determine the *E.M.F.* of the cell containing it and the reference electrode. In the earlier investigations † a Compton or a Lindemann electrometer was employed as null instrument in an ordinary potentiometer system, subsequently the ballistic galvanometer, in conjunction with a condenser, was used for the same purpose ‡ or else its throw was standardized by means of solutions of known *pH*,§ but more

recently a large number of thermionic-valve circuits have been devised which permit of the measurement of the *E.M.F.* of high-resistance cells without difficulty.|| The potential of the glass electrode is related to the hydrogen ion activity of the solution in which it is immersed by the usual hydrogen electrode equation, thus

$$\pi = k + \frac{RT}{F} \ln a_{\text{H}}. \quad (\text{xlii})$$

* Hughes (W. S.), *J. Chem. Soc.*, 1928, 491; Elder, *J. Amer. Chem. Soc.*, 1929, 51, 3266; MacInnes and Dole, *ibid.*, 1930, 52, 29; Sokolov and Passinski, *Z. physikal. Chem.*, 1932, 160, 366.

† Hughes (W. S.), *J. Amer. Chem. Soc.*, 1922, 44, 2860; Kerridge, *J. Sci. Inst.*, 1926, 3, 404; Elder, *J. Amer. Chem. Soc.*, 1929, 51, 3266; MacInnes and Belcher, *ibid.*, 1931, 53, 3315.

‡ Jones (G.) and Kaplan, *ibid.*, 1928, 50, 1845; Dole, *ibid.*, 1931, 53, 620; Bennowitz and Kellner, *Z. anal. Chem.*, 1935, 102, 1.

§ Cf. Morton, *J. Chem. Soc.*, 1934, 256.

|| For references, see the summaries given by Glasstone, *Ann. Report Chem. Soc.*, 1933, 30, 283; Müller (F.) and Dürichen, *Z. Elektrochem.*, 1935, 41, 559; 1936, 42, 31, 730; Schwabe, *ibid.*, 1935, 41, 681; Bromley, *Analyst*, 1935, 60, 533.

The value of k depends on the nature of the glass and on the experimental arrangement; it is determined for the particular electrode by measurements in buffer solutions of known pH . The potential follows equation (xlii) closely over the range of pH from 0 to 9, and approximately up to pH 12; * in very acid or in alkaline solutions deviations are observed, and under the latter conditions the results are influenced by the nature of the cations present in the solution.† The glass electrode can be used in the presence of oxidizing agents and of organic compounds which poison the hydrogen gas electrode and make the quinhydrone electrode inapplicable, but it does not function satisfactorily in pure ethyl alcohol, in acetic acid or in the presence of gelatin. Other advantages of the glass electrode are that it can be employed in unbuffered media, it comes to equilibrium rapidly and can be adapted to measure the pH of a very small amount of solution: the chief disadvantages, apart from those mentioned above, are connected with the technique of measuring the *E.M.F.* of the high-resistance cell.‡

The functioning of the glass electrode as an indicator of hydrogen ion concentrations is probably due to the fact that the glass acts as a membrane permeable only to hydrogen ions, in the range over which equation (xlii) is applicable. The glass electrode potential is then ideally a liquid junction potential between the two electrolytes, one inside and one outside, only the hydrogen ion being capable of moving across the junction. If the mobility of the anion is put equal to zero in any of the equations already given for the liquid junction potential, it will be seen that they reduce to the form §

$$\pi_d = \frac{RT}{F} \ln \frac{[H]_1}{[H]_2}$$

* Hughes, *loc. cit.*, 1928; MacInnes and Belcher, *loc. cit.*

† Horovitz, *Z. Physik*, 1923, 15, 369; *Z. physikal. Chem.*, 1925, 115, 424; Schiller, *Ann. Physik*, 1924, 74, 105; Hughes, *loc. cit.*, 1928; Dole, *J. Amer. Chem. Soc.*, 1931, 53, 4260; 1932, 54, 3095; Buchböck, *Z. physikal. Chem.*, 1931, 156, 232; Urban and Steiner, *J. Physical Chem.*, 1931, 35, 3058; Sokolov and Passinski, *loc. cit.*

‡ For references to properties and applications of the glass electrode, see summaries by Glasstone, *loc. cit.*; Schwabe, *loc. cit.*; Kilde, *Dansk. Tidsskr. Farm.*, 1935, 9, 129; also, Lang, *J. Amer. Chem. Soc.*, 1934, 56, 1034 (trustworthiness); Neuss and Rieman, *ibid.*, p. 2238 (oxidizing solutions); Ellis and Kiehl, *ibid.*, 1935, 57, 2139; Schwabe, *Z. Elektrochem.*, 1936, 42, 147 (unbuffered solutions). For various forms of the electrode itself, see Kerridge, *loc. cit.*; MacInnes and Dole, *Ind. Eng. Chem. (Anal.)*, 1929, 1, 57; MacInnes and Belcher, *ibid.*, 1933, 5, 199; Morton, *J. Chem. Soc.*, 1932, 2469.

§ This is not strictly correct, since there is always found in practice an 'asymmetry potential,' so that even when the same electrolyte is inside and outside the glass electrode the potential is not zero.

where $[H']_1$ and $[H']_2$ represent the hydrogen ion concentrations (or activities) in the two solutions; since one of these, inside the glass bulb, is a constant it follows that the glass electrode potential will be the normal logarithmic function of the hydrogen ion concentration of the external solution. The deviations in highly acid solutions have been attributed to the fact that the hydrogen ion is hydrated (cf. p. 179) and the free energy of the transport of water, the activity of which is very different on the two sides of the glass membrane, is added to that for the transfer of the hydrogen ions. In alkaline media the cations, being present in amounts greatly in excess of the hydrogen ions, are effective in the transport of electricity through the glass, and so the electrode potential is no longer dependent on the pH only, but is influenced by the nature and concentration of the cations present.*

Oxide Electrodes—An electrode consisting of a metal and its oxide, or of an unattackable metal, e.g. platinum, in contact with a higher and lower oxide, may be regarded as an oxygen electrode with the gas at a pressure equal to the dissociation pressure of the oxide. Since the potential of any oxygen (or oxide) electrode is expressed by the equation (p. 333)

$$\pi = k + \frac{RT}{F} \ln a_H. \quad (\text{xliia})$$

such electrodes may be used as indicators of hydrogen ion activity; the value of the constant k for the particular oxide is determined by measurements in solutions of known pH. In order that an oxide electrode shall be suitable for this purpose the oxide must be sparingly soluble in solutions of all hydrogen ion concentrations, and the metal must not displace hydrogen from solution. The most satisfactory electrode of this type is one consisting of antimony and antimony trioxide, $Sb | Sb_2O_3$; there is generally sufficient oxide on the surface of cast antimony for its addition not to be necessary. The antimony electrode behaves reversibly, according to equation (xliia), over the pH range of 2 to 7, but in more alkaline solutions deviations occur; it is not readily poisoned, and since no special technique is required for measurement of the potential it is finding increasing application.†

* Dole, *J. Amer. Chem. Soc.*, 1931, **53**, 4260; 1932, **54**, 2120, 3095; *J. Chem. Physics*, 1934, **2**, 862; see also, Halpern and Gross (P.), *ibid.*, p. 184; Zirkler, *Z. Physik*, 1932, **77**, 126; Haugaard, *Z. physikal. Chem.*, 1932, **160**, 279.

† Uhl and Kestranek, *Monatsh.*, 1923, **44**, 29; Kolthoff and Hartong, *Rec. trav. Chim.*, 1925, **44**, 113; Roberts and Fenwick, *J. Amer. Chem. Soc.*, 1928, **50**, 2125; Shukov *et al.*, *Z. Elektrochem.*, 1929, **35**, 349, 853; 1931, **37**, 771; for summaries with references, see Parks and Beard, *J. Amer. Chem. Soc.*, 1932, **54**, 856; Glasstone, *loc. cit.*; also, Tomiyama,

The antimony electrode has also been used in non-aqueous solutions.*

The use of a tungsten-manganic oxide electrode for determining pH 's has been suggested by H. C. Parker; † the tungsten acts as the non-attackable electrode, whereas the manganic oxide is the 'higher oxide' with a definite oxygen pressure. A tungsten wire, presumably covered with a film of oxide, behaves as a hydrogen electrode but it is not strictly reversible. ‡ Similar electrodes resistant to 'poisoning' have been devised and developed for use in the control of industrial processes.§

Application of Hydrogen Electrodes—The hydrogen electrode, in one form or another, can be applied to the study of hydrolysis of salts (p. 207), to the determination of hydrogen ion 'activities' of buffer solutions (p. 237), and to checking the pH values corresponding to the colour changes of indicators; it may also be used for evaluating the dissociation constants of acids and bases. Various formulæ have been deduced connecting the hydrogen ion activity of a partially neutralized solution with the relative amounts of acid and base added, and their dissociation constants (Chap. IX); if the extent of neutralization is known and the hydrogen ion activity determined by means of a hydrogen gas, or quinhydrone, electrode the value of the dissociation constant may be calculated. This provides a valuable method for the determination of these constants, particularly for polybasic acids and polyacid bases. ¶ An alternative procedure devised and used by Harned and

J. Biochem. Japan, 1933, 18, 285; Pieper, *Z. Elektrochem.*, 1934, 40, 793; for general theory, see Wulff *et al.*, *ibid.*, 1935, 41, 542; Bodforss and Holmqvist, *Z. physikal. Chem.*, 1932, 161, 61; Holmqvist, *Svensk. Kim. Tidsk.*, 1934, 46, 2; 1935, 47, 102.

* Halford, *J. Amer. Chem. Soc.*, 1931, 53, 2944; 1933, 55, 2272; Tomiček and Feldmann, *loc. cit.*

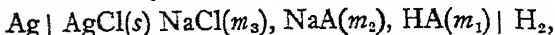
† *Ind. Eng. Chem.*, 1925, 17, 737.

‡ Britton and Dodd, *J. Chem. Soc.*, 1931, 829; Jofa and Petrov, *Zavod. Lab.*, 1934, 3, 728.

§ See Parker (H. C.) and Dannerth, *Ind. Eng. Chem.*, 1925, 17, 637; also Baylis, *ibid.*, 1923, 15, 852.

¶ Noyes, *Z. physikal. Chem.*, 1893, 11, 495; Smith (W. A.), *ibid.*, 1898, 25, 193; McCoy, *J. Amer. Chem. Soc.*, 1908, 30, 688; Walpole, *J. Chem. Soc.*, 1914, 105, 2521; Datta and Dhar, *ibid.*, 1915, 107, 824; Paul, *Z. Elektrochem.*, 1915, 21, 552; 1917, 23, 70; *Z. physikal. Chem.*, 1924, 110, 417; Drucker, *ibid.*, 1920, 96, 381; *Z. Elektrochem.*, 1920, 26, 364; Michaelis and Krüger, *Biochem. Z.*, 1921, 119, 307; Larsson, *Z. anorg. Chem.*, 1922, 125, 281; 1926, 155, 247; *Z. physikal. Chem.*, 1931, 156, 352, 381; Auerbach and Smolczyk, *ibid.*, 1924, 110, 83; Britton, *J. Chem. Soc.*, 1924, 125, 423; 1925, 127, 1896; Prideaux *et al.*, *ibid.*, 1924, 125, 423; 1927, 2164; Ingold and Gane, *ibid.*, 1928, 1594; 1931, 2156; Duboux and Frommelt, *J. Chim. physique*, 1927, 24, 245; Cohn *et al.*, *J. Amer. Chem. Soc.*, 1928, 50, 696; Kirschmann, *ibid.*, 1930, 52, 23; Sihvonen, *Z. Elektrochem.*, 1930, 36, 165; Hahn and Klockmann, *Z.*

his collaborators* permits of the determination of dissociation constants by means of cells which do not involve liquid junction potentials, whereas those depending on the direct measurement of hydrogen ion activity presupposes their complete elimination, always a matter of uncertainty. The *E.M.F.* of the cell

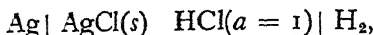


containing the acid HA and its sodium salt at the concentrations indicated, is given by

$$E = E_0 - \frac{RT}{F} \ln a_{\text{H}^+} a_{\text{Cl}^-} \quad \text{. . . (xliii)}$$

$$= E_0 - \frac{RT}{F} \ln [\text{H}^+] [\text{Cl}^-] f_{\text{H}^+} f_{\text{Cl}^-} \quad \text{. . . (xliiia)}$$

where E_0 is the *E.M.F.* of the cell



with hydrochloric acid at unity activity; as already seen (p. 364), the value of E_0 is 0.2222 volt at 25°. The thermodynamic dissociation constant of the acid HA is

$$K = \frac{a_{\text{H}^+} \times a_{\text{A}^-}}{a_{\text{HA}}} = \frac{[\text{H}^+] [\text{A}^-] f_{\text{H}^+} f_{\text{A}^-}}{[\text{HA}] f_{\text{HA}}} \quad \text{. . . (xliv)}$$

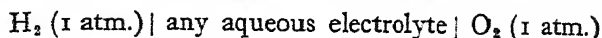
and from equations (xliiia) and (xliv) it can be readily shown that

$$E - E_0 + \frac{RT}{F} \ln \frac{[\text{HA}] [\text{Cl}^-]}{[\text{A}^-]} = - \frac{RT}{F} \ln \frac{f_{\text{H}^+} f_{\text{Cl}^-} f_{\text{HA}}}{f_{\text{H}^+} f_{\text{A}^-}} - \frac{RT}{F} \ln K \quad \text{(xlv)}$$

If E is measured, and E_0 is known, the left-hand side of this equation can be evaluated for various concentrations of acid, salt and sodium chloride; $[\text{Cl}^-]$ is taken as equal to m_s , $[\text{HA}]$ is given by $m_1 - [\text{H}^+]$, and $[\text{A}^-]$ is $m_2 + [\text{H}^+]$, a sufficiently accurate value of $[\text{H}^+]$ being calculated from an approximate dissociation constant. The resulting quantities are plotted against the ionic strength (μ), and when extrapolated to $\mu = 0$, the intercept gives $-RT/F \ln K$, since at infinite dilution the activity coefficient fraction in equation (xlv) becomes unity and its logarithm is zero. This is probably the most accurate method for determining the true dissociation constants of acids: it has also been used for bases and ampholytes.

physikal. Chem., 1931, 157, 206, 209; Morton, *Trans. Faraday Soc.*, 1928, 24, 14; Partington *et al.*, *ibid.*, 1934, 30, 598; 1935, 31, 922; Ogston and Brown (J. F.), *ibid.*, p. 574; Vogel (A. I.) *et al.*, *J. Chem. Soc.*, 1935, 1624; Glasstone *et al.*, *ibid.*, p. 1821; Bode, *Z. physikal. Chem.*, 1934, 170, 231; Goodhue and Hixon, *J. Amer. Chem. Soc.*, 1935, 57, 1688.
* *Ibid.*, 1930, 52, 5079, 5091; 1932, 54, 1350; 1933, 55, 1946; 1934, 56, 24, 314, 1042, 1695, 2039; 1935, 57, 1669; also MacInnes *et al.*, *ibid.*, 1933, 55, 2630; 1935, 57, 1683; Roberts (E. J.), *ibid.*, 1934, 56, 878.

Ionic Product of Water *—The *E.M.F.* of the reversible cell

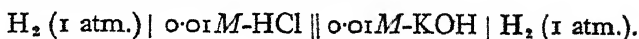


should be given by

$$= \left(\pi_{\text{H}, \text{H}'} + \frac{RT}{F} \ln a_{\text{H}'} \right) - \left(\pi_{\text{O}, \text{OH}'} - \frac{RT}{F} \ln a_{\text{OH}'} \right) \quad (\text{xlvi})$$

$$\pi_{\text{H}, \text{H}'} - \pi_{\text{O}, \text{OH}'} + \frac{RT}{F} \ln (a_{\text{H}'} \times a_{\text{OH}'})$$

where $\pi_{\text{H}, \text{H}'}$ and $\pi_{\text{O}, \text{OH}'}$ are the standard electrode potentials of hydrogen and oxygen respectively, at one atmosphere pressure, and $a_{\text{H}'}$ and $a_{\text{OH}'}$ are the respective activities. If E were measured the value of $a_{\text{H}'} \times a_{\text{OH}'}$ (i.e. K_w) could be determined; unfortunately the oxygen electrode is not reversible and the method is not satisfactory. An alternative procedure is based on the determination of the *E.M.F.* of the cell



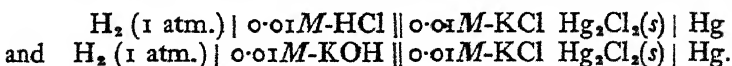
This *E.M.F.* (E), free from liquid junction potential, is

$$E = \frac{RT}{F} \ln \frac{a_{\text{H}'}'}{a_{\text{H}'}''} \quad (\text{xlvii})$$

where $a_{\text{H}'}'$ and $a_{\text{H}'}''$ represent the activities of hydrogen ions in the acid and alkaline solutions respectively. Since $a_{\text{H}'}'' \times a_{\text{OH}'}''$ equals K_w , where $a_{\text{OH}'}''$ is the hydroxyl ion activity in the alkaline solution,

$$E = \frac{RT}{F} \ln \frac{a_{\text{H}'}' a_{\text{OH}'}'}{K_w} \quad (\text{xlviiii})$$

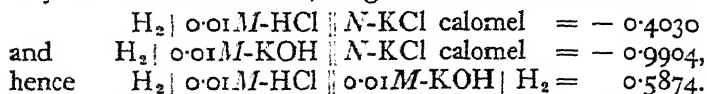
The *E.M.F.* of the cell is not necessarily measured directly, but the value may be calculated from measurements of such cells as:



The electrode potential of the right-hand half-element can be determined by measurement against a standard (e.g. 0.1*N*-KCl) calomel electrode, allowance being made for liquid junction potential; hence the potentials of the two hydrogen electrodes, in 0.01*M*-HCl and 0.01*M*-KOH respectively, together with the corresponding liquid junction potentials can be evaluated. The magnitude of the latter

* Ostwald, *Z. physikal. Chem.*, 1893, **11**, 521; Nernst, *ibid.*, 1894, **14**, 155; Löwenherz, *ibid.*, 1896, **20**, 283; Lorenz and Böhi, *ibid.*, 1909, **66**, 733; Sørensen, *Biochem. Z.*, 1909, **21**, 131; Lewis, Brighton and Sebastian, *J. Amer. Chem. Soc.*, 1917, **39**, 2245. For the ionic product of D_2O , by this method, see Wynne-Jones, *Trans. Faraday Soc.*, 1936, **32**, 1397.

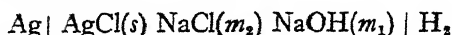
may be calculated by the Lewis and Sargent* formula and the true hydrogen electrode potentials found. From these results the *E.M.F.* of the required cell, free from liquid junction potentials, may be obtained. Lewis, Brighton and Sebastian found at 25°:



If the activity coefficients of hydrogen and hydroxyl ions in 0.01*M* strong acid and alkali, respectively, are assumed to be 0.930, the values of a_{H}' and a_{OH}'' are each 0.0093; hence

$$\begin{aligned} 0.5874 &= 0.0591 \log (0.0093)^2 - 0.0591 \log K_w \\ \therefore K_w &= 1.01 \times 10^{-14} \text{ at } 25^\circ. \end{aligned}$$

The method just considered suffers from the weakness of all procedures involving the elimination of liquid junction potentials: it is of interest, therefore, to describe a means for determining the ionic product of water in which such potentials are not involved.† The *E.M.F.* of the cell



which is exactly analogous to those used by Harned, mentioned above (p. 386), may be written, as before,

$$E = E_0 - \frac{RT}{F} \ln a_{\text{H}} a_{\text{Cl}}' \quad (\text{xlix})$$

$$= E_0 - \frac{RT}{F} \ln K_w - \frac{RT}{F} \ln \frac{a_{\text{Cl}}'}{a_{\text{OH}}'} \quad (\text{xlixa})$$

$$= E_0 - \frac{RT}{F} \ln K_w - \frac{RT}{F} \ln \frac{[\text{Cl}']}{[\text{OH}']} - \frac{RT}{F} \ln \frac{f_{\text{Cl}}'}{f_{\text{OH}}'} \quad (\text{xlixb})$$

It is evident, therefore, that if $E - E_0 + RT/F \ln [\text{Cl}']/[\text{OH}]$, where E is the measured *E.M.F.* of the cell, E_0 has the same significance as previously, i.e. 0.2222 volt at 25°, and $[\text{Cl}']$ and $[\text{OH}']$ are equal to m_2 and m_1 respectively, is plotted against the ionic strength and the straight line extrapolated to infinite dilution the intercept gives $-RT/F \ln K_w$. The value for K_w obtained in this way was $0.988 \pm 0.004 \times 10^{-14}$ at 25°.

Electrometric Titration ‡—One of the most important appli-

* *J. Amer. Chem. Soc.*, 1909, **31**, 363; *vide supra*, p. 316.

† Roberts (E. J.), *ibid.*, 1930, **52**, 3877; see also Abel, Bratu and Redlich, *Z. physikal. Chem.*, 1935, **173**, 353 for D_2O . For the determination of the ionic concentration product by means of cells without liquid junction see references to the work of Harned and collaborators, p. 213 *supra*.

‡ For reviews, see Kolthoff and Furman, *Potentiometric Titrations*, 1931; Furman, *Ind. Eng. Chem. (Anal.)*, 1930, **2**, 213; Taylor, *Physical Chemistry*, 1931, Chap. XIII (Furman); Glasstone, *Ann. Reports Chem. Soc.*, 1933, **30**, 283; Sutton, *Volumetric Analysis*, 1935, Part V (Glasstone). References to simplified methods of titration will be found therein.

cations of the hydrogen electrode is in connection with the electrometric titration of acids and bases. It has been shown (p. 217) that during titration the *pH* of an acid or an alkaline solution generally alters very suddenly in the vicinity of the equivalence point; since the potential of a hydrogen electrode gives a direct measure of *pH*,* this potential will change markedly at the equivalence point. The application of the hydrogen electrode to determine the end-point of a neutralization reaction was first made by Böttger,† who used the ordinary Poggendorff method to measure potentials; the technique was much simplified when Hildebrand ‡ applied the

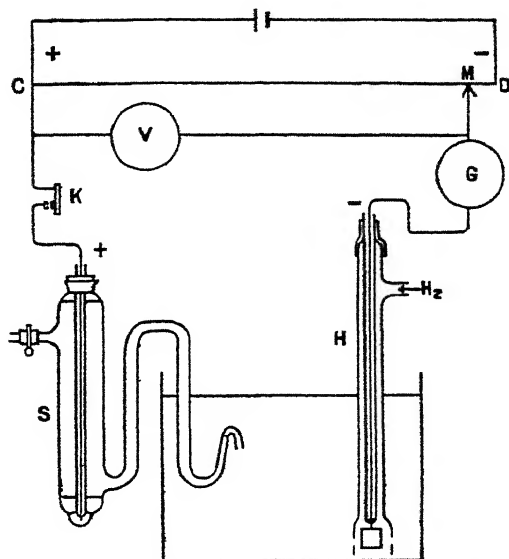


FIG. 27.—Potentiometer-voltmeter method for hydrogen electrode

potentiometer-voltmeter method.§ An accumulator *A* (Fig. 27) is connected across a resistance *CD*, the positive end *C* being joined to the standard calomel electrode *S* through a key *K*. The hydrogen electrode *H*, dipping in the acid solution to be titrated, is connected through a galvanometer *G* to the movable contact *M*; the millivoltmeter *V* measures the fall of potential between *C* and *M*. If the

* $\pi_H = RT/F (\ln a_{H^+}) = -2.3 RT/F (pH)$.

† *Z. physikal. Chem.*, 1897, 24, 253.

‡ *J. Amer. Chem. Soc.*, 1913, 35, 847.

§ See Sand, *J. Chem. Soc.*, 1907, 91, 380; *J. Soc. Chem. Ind.*, 1911, 30, 3T.

position of M is so adjusted that no current flows through the galvanometer G when the key K is depressed, then the $E.M.F.$ of the cell made up of S and H is just balanced by the opposing $E.M.F.$ tapped off from the accumulator A ; the value of this $E.M.F.$, and hence that of the cell $S - H$, is indicated on the voltmeter V . Alkali is added gradually to the acid solution and the $E.M.F.$ measured after each addition; if an $E.M.F.$ -titration curve is plotted it should be almost identical in shape with the pH -neutralization curves already described (Chap. IX). The end-point of the titration can be determined by the position of the inflexion in the curve: to do this accurately the quantity $\Delta E/\Delta v$ should be plotted against the amount of the titrant added, ΔE being the change of potential resulting from the addition of a definite small increment Δv , e.g. one drop of titrant. Hence $\Delta E/\Delta v$ is a measure of the slope of the titration curve; as this slope is a maximum at the end-point, the latter may be determined by observing the volume of titrant added when $\Delta E/\Delta v$ is a maximum.* Strictly speaking it is only for the titration of a strong acid by a strong base that the maximum value of $\Delta E/\Delta v$ coincides exactly with the equivalence point; when a weak acid is neutralized by a strong base the pH at the point for which $\Delta E/\Delta v$ is a maximum is less than at the equivalence point by $0.65 \sqrt{K_w/cK_a}$, where c is the acid concentration and K_w and K_a are the ionic product of water and the dissociation constant of the acid, respectively. The stronger the acid and the greater its concentration, therefore, the smaller the error: provided cK_a is greater than 10^{-10} this error is not serious. The accuracy with which the position of maximum $\Delta E/\Delta v$ can be estimated depends on its magnitude; the smaller are c and K_a the smaller is the value of $\Delta E/\Delta v$, and if cK_a is less than $27K_w$ there is no inflexion in the curve and it is impossible to detect the end-point.†

A simple but ingenious method of 'differential titration' was devised by Cox.‡ The quantity $\Delta E/\Delta v$ represents the change of potential for a given addition of titrant, and it may be measured by the difference of potential between similar electrodes in two solutions to one of which has been added Δv more titrant than to the other; when this difference of potential reaches a maximum, $\Delta E/\Delta v$ is a maximum and the end-point is attained. Cox divided

* Hostetter and Roberts (H. S.), *J. Amer. Chem. Soc.*, 1919, **41**, 1337; see also, Hahn and Frommer, *Z. physikal. Chem.*, 1927, **127**, 1; Hahn, *ibid.*, 1930, **146**, 363.

† Eastman, *J. Amer. Chem. Soc.*, 1925, **47**, 332; 1928, **50**, 418; 1934, **56**, 2646; Roller, *ibid.*, 1928, **50**, 1; 1932, **54**, 3485; 1935, **57**, 98; Kilpi, *Z. physikal. Chem.*, 1935, **173**, 223; 1935, **174**, 441; 1935, **175**, 239.

‡ *J. Amer. Chem. Soc.*, 1925, **47**, 2138.

the solution to be titrated into two equal parts; into each was placed a suitable hydrogen electrode and electrical connection was made between the two solutions by wet filter-paper. The electrodes were connected to a millivoltmeter or galvanometer so that any difference of potential could be indicated. Titrant was added from two similar burettes to the two solutions, one burette being always 0.2 c.c. in advance of the other; when the potential difference was a maximum the total titrant added was regarded as equivalent to the total titrated solution. This method of differential titration eliminates the necessity of plotting curves and the use of a calomel electrode is avoided. In a modified differential method* two similar electrodes are placed in the same solution, but by means of special devices a small quantity of the titrated solution surrounding one of the electrodes is temporarily kept from mixing with the bulk of the solution until after each addition of titrant. The potential difference between the two electrodes is a measure of $\Delta E/\Delta v$, and is a maximum at the end-point. Thermionic valve-circuits have been devised for the continuous measurement of E.M.F. for electrometric titration purposes: by means of suitable modifications these may be adapted to act as differential titration meters.†

The hydrogen gas electrode has been used for many titrations,‡ some of them of industrial importance; § with coloured solutions, when ordinary indicators are valueless, electrometric titration can be quite satisfactory. Oxygen gas or air electrodes have been used for titration purposes,|| and so also have the quinhydrone,** glass,†† and antimony electrodes.‡‡ Titrations may also be performed using a bright platinum electrode, without the necessity of passing

* MacInnes and Jones (P. T.), *ibid.*, 1926, 48, 2831.

† See, Glasstone, *Ann. Reports Chem. Soc.*, 1933, 30, 292, for full references; Clarke and Wooten, *J. Physical Chem.*, 1929, 33, 468 give a discussion of the theory of differential titration.

‡ See Kolthoff and Furman, *op. cit.*

§ Keeler, *J. Ind. Eng. Chem.*, 1922, 14, 395; Klopsteg, *ibid.*, 399.

|| See references on p. 378 *supra*.

** Kolthoff, *Rec. trav. chim.*, 1923, 42, 186; La Mer and Parsons, *loc. cit.*; Harris, *J. Chem. Soc.*, 1923, 123, 3294; Auerbach and Smolczyk, *loc. cit.*; Rasmussen, *Z. Elektrochem.*, 1925, 31, 189; Niklas and Hock, *Z. angew. Chem.*, 1925, 38, 407; Klit, *Z. physikal. Chem.*, 1927, 131, 61; Rabinowitsch and Kargin, *Z. Elektrochem.*, 1928, 34, 311; Prideaux, *J. Soc. Chem. Ind.*, 1929, 48, 87 T.

†† E.g. Horovitz, *loc. cit.*; Hughes, *loc. cit.*; Partridge, *J. Amer. Chem. Soc.*, 1929, 51, 1; Kargin, *Z. anorg. Chem.*, 1929, 183, 77; Britton and Robinson, *Trans. Faraday Soc.*, 1932, 28, 531.

‡‡ Kolthoff and Hartong, *loc. cit.*; Britton and Robinson, *J. Chem. Soc.*, 1931, 458; Malvea and Withrow, *J. Amer. Chem. Soc.*, 1932, 54, 2243.

hydrogen or oxygen; * other electrodes of a similar type have been devised.†

Other Electrometric Titrations—Observations of electrode potential can be used for the determination of the end-points of reactions other than those involving neutralizations; precipitation reactions may be followed electrometrically and so also may oxidation-reduction processes.‡ Consider the titration of a solution containing a salt (MX) of the cation M' with a salt (BA) of the anion A' , where MA is sparingly soluble, e.g. silver nitrate ($M' = Ag'$) with sodium chloride ($A' = Cl'$). Let c gm. mols. per litre be the initial concentration of the salt MX, and at any instant during the titration let x gm. mols. of BA have been added per litre; suppose y gm. mols. per litre is the solubility of the sparingly soluble salt MA at this instant. If the salts are assumed to be completely ionized then $[M'] = c - x + y$, where $c - x$ is due to unchanged MX and y to the MA remaining in solution; further, $[A'] = y$, since the remainder of the A' ions added are removed in the precipitate. Taking ionic activity coefficients as unity,

$$a_{M'} \times a_{A'} = (c - x + y)y = \text{constant } (k_s)$$

where k_s is the solubility product of the salt. If an electrode of the metal M , reversible with respect to M' ions, were placed in the solution during titration its potential would be given by

$$\pi = \pi_0 + \frac{RT}{nF} \ln a_{M'} \quad (I)$$

$$\approx \pi_0 + \frac{RT}{nF} \ln (c - x + y) \quad \dots \quad (Ia)$$

If k_s is known, then the variation of electrode potential during the course of a titration may be calculated. At the equivalence point $c = x$, hence

$$\pi = \pi_0 + \frac{RT}{nF} \ln y = \pi_0 + \frac{RT}{nF} \ln \sqrt{k_s} \quad (II)$$

Should the solution of BA be added beyond this point the value of $[A']$ becomes $x - c + y$, whereas $[M']$ becomes equal to y , the conditions being equivalent to the titration of BA by the gradual addition of MX. In these circumstances $y(x - c + y)$ is equal to

* van der Meulen and Wilcoxon, *Ind. Eng. Chem.*, 1923, 15, 62.

† Baylis, *ibid.*, p. 852; Brunnich, *ibid.*, 1925, 17, 631; Willard and Boldyreff, *J. Amer. Chem. Soc.*, 1929, 51, 471; Fuoss, *Ind. Eng. Chem. (Anal.)*, 1929, 1, 125; Closs and Kahlenberg, *Trans. Amer. Electrochem. Soc.*, 1928, 54, 369; Müller (E.) and Kogert, *Z. physikal. Chem.*, 1928, 136, 437; Banchetti, *Gazzetta*, 1932, 62, 999, 1011; Britton and Dodd, *loc. cit.*; Furman and Low, *J. Amer. Chem. Soc.*, 1933, 55, 1310.

‡ Behrend, *Z. physikal. Chem.*, 1893, 11, 482; Crotochino, *Z. anorg. Chem.*, 1900, 24, 225.

k_s , and the variation of electrode potential may again be calculated. It is thus possible to determine theoretically, from a knowledge of the solubility product, the whole course of the electrode potential-titration curve for a precipitation reaction; * in general it is found that the curve shows a marked inflexion in the vicinity of the equivalence point, and that the slope $d\pi/dx$ is greatest at this point. The end-point of a titration may thus be determined by measurement of electrode potentials. If the two solutions titrated are of equivalent concentrations the electrode potential-titration curve will be symmetrical in the vicinity of the equivalence point, but if the concentrations (or valencies) are different, there will be a dissymmetry and $d\pi/dx$ will not be greatest *exactly* at the equivalence point; for very accurate work only, however, is a correction necessary.†

The general conclusions concerning the titration curve may be reached by differentiating the expression for π with respect to x ; thus

$$d\pi/dx = -k/(c-x+2y) \quad \text{. (lii)}$$

and
$$d^2\pi/dx^2 = -k(c-x)/(c-x+2y)^3 \quad \text{. . . (liii)}$$

When $d\pi/dx$ is a maximum, $d^2\pi/dx^2$ is zero and $c=x$, which is the condition for the equivalence point. Further, since $(c-x+y) = k_s/y$,

$$d\pi/dx = -ky/(k_s+y)^2 \quad \text{. (liv)}$$

$$= -k/2\sqrt{k_s} \text{ at the equivalence point; . . . (liva)}$$

hence $d\pi/dx$, i.e. the potential change during titration, is greater the smaller the solubility product k_s . In a titration involving the precipitation of an unsymmetrical salt of the type M_2A (or MA_2), the potential-titration curve is not symmetrical, and it may be shown that the maximum for $d\pi/dx$ is not reached at the equivalence point; the deviations are, however, inappreciable if the solubility product of the precipitate is small and the reacting solutions are not too dilute.‡ The addition of alcohol, which decreases the solubility of the precipitate, is often advantageous.

Behrend § studied the electrometric titration of halides with silver and with mercurous salts, using silver and mercury reference elec-

* Volume changes are neglected and activity coefficients are taken as unity throughout, but the general conclusions reached are not thereby invalidated.

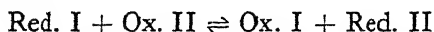
† Hahn *et al.*, *Z. physikal. Chem.*, 127, 1; 1928, 133, 390; Lange (E.) *et al.*, *ibid.*, 129, 111; *Z. Elektrochem.*, 1930, 36, 171; 980; see also Brown (A. S.) and MacInnes, *J. Amer. Chem. Soc.*, 1935, 57, 459; Kolthoff and Lingane, *ibid.*, 1936, 58, 1254.

‡ See Kolthoff and Furman, *Potentiometric Titrations*, 1931, p. 18 *et seq.*; cf. also, Ringbom, *Z. physikal. Chem.*, 1935, 173, 198.

§ *loc. cit.*

trodes, respectively; he showed that the method could also be used for estimating mixtures of halides.* Cyanides, sulphocyanides, ferrocyanides, sulphides and thiosulphates may be titrated with the aid of a silver electrode, whereas the mercury electrode has found special application in the analysis of sulphide solutions; copper, nickel and cobalt have also been used as reference electrodes.† Instead of using as electrode the metal whose ions were being titrated, Dutoit and von Weisse ‡ employed as indicator a platinum cathode polarized by means of a very small current. For electro-metric titration purposes a silver electrode may often be replaced by one of platinum, palladium or gold.§ The bi-metallic polarized electrode system of Willard and Fenwick || has been applied by these authors to replace the ordinary reference electrode in precipitation reactions. A minute current, of the order of 10^{-6} amp., is passed between two small similar electrodes placed in the titrated solution; the potential difference between the anode and cathode thus formed is measured by a potentiometer. An abrupt change is observed at the end-point of the titration just as if a simple electrode, e.g. silver, were being used in conjunction with a standard calomel electrode. By using suitable pairs of different metals, similar results may be obtained without the passage of current from an external source: these are generally known as un-polarized bimetallic electrode systems.**

Oxidation-Reduction Titrations—An unattackable electrode in an oxidation-reduction system attains a potential dependent on the relative amounts of oxidized and reduced forms present in solution. In the vicinity of the end-point of a titration the ratio of oxidized to reduced form changes very rapidly; hence there will be a marked inflexion in the electrode potential-titration curve by means of which the position of the end-point may be determined. Suppose c gm. mols. per litre is the concentration of a reduced form (Red. I) which is titrated by means of an oxidizing agent (Ox. II), so that the reaction



* Cf. Dutoit and von Weisse, *J. Chim. phys.*, 1911, 9, 578; Britton, *Analyst*, 1925, 50, 601; Clark (W.), *J. Chem. Soc.*, 1926, 749; Lange and Schwartz, *Z. Elektrochem.*, 1926, 32, 240.

† Kolthoff and Furman, *op. cit.*; Spencer and Pring, *Analyst*, 1929, 54, 509, 576; Glasstone and Speakman, *ibid.*, 1930, 55, 93.

‡ *Loc. cit.*

§ Müller (E.), *Z. Elektrochem.*, 1924, 30, 419; see also Böttger and Schall, *Z. physikal. Chem.*, 1933, 165, 398.

|| *J. Amer. Chem. Soc.*, 1922, 44, 2516; 1923, 45, 623; van Name and Fenwick, *ibid.*, 1925, 47, 9.

** *Idem.*, *ibid.*, p. 19; Atanasiu and Velculesco, *Z. anal. Chem.*, 1931, 85, 120; Hiltner, *Chem.-Ztg.*, 1933, 57, 704.

occurs. At any instant, when x gm. mols. of Ox. II have been added per litre of solution, let $c - y$ be the concentration of Red. I remaining un-oxidized; the concentrations of Ox. I, Red. II and Ox. II are therefore y , y and $x - y$ respectively. Since the system is in equilibrium, then (neglecting activity coefficients)

$$k = \frac{[\text{Ox. I}][\text{Red. II}]}{[\text{Red. I}][\text{Ox. II}]} = \frac{y^2}{(c - y)(x - y)} \quad (\text{lv})$$

and the oxidation-reduction potential is given by

$$\pi = \pi_{0\text{II}} + \frac{RT}{nF} \ln \frac{x - y}{y} \quad (\text{lvi})$$

By means of these equations it is possible to calculate the electrode potential at any stage of the titration, provided the equilibrium constant k is known. If the titration-potential curve is plotted it will be found that, provided k is large, there is a sharp break at the titration equivalence point.* The same conclusions may be reached by a simple mathematical treatment; differentiating the expression for π with respect to x , it follows that (replacing RT/nF by k_1)

$$d\pi/dx = k_1 c / (2cx - cy - xy) \quad (\text{lvii})$$

and $d^2\pi/dx^2$

$$= k_1 c \{c(2c - y)(x - c) + 2(c - y)^2(x + c)\} / (2cx - cy - xy)^3 \quad (\text{lviii})$$

When $d\pi/dx$ is a maximum, $d^2\pi/dx^2$ is zero, but c is *not* then equal to x ; the inflexion in the electrode potential-titration curve cannot therefore coincide with the equivalence point unless

$$\frac{2(c - y)^2(x + c)}{c(2c - y)} \text{ is equal to } 0.$$

This term must have a positive value, but it is almost negligibly small if the value of k , the equilibrium constant, is large; if this is the case then the difference between c and x at the point of inflexion will be very small and a reasonably accurate titration may be performed electrometrically. Further, it may be shown that $d\pi/dx$ increases as c and k increase; hence when k is large the inflexion not only occurs very close to the equivalence point, but it is also very marked. If k is small the titration cannot be carried out accurately since the inflexion is small, and in any case it is appreciably removed from the true end-point.†

* A large value of k means that the standard oxidation-reduction potentials of the systems I and II are appreciably different (see p. 399); as already observed (p. 349), under these conditions a marked inflexion of potential is to be expected at the equivalence point.

† If the oxidation-reduction system involves more than one molecule of each reactant or resultant the mathematical treatment is more complicated; the titration curves are unsymmetrical but the same general conclusions are applicable as to the simple case.

Electrometric titrations involving oxidation-reduction reactions were first performed by Crotonino,* and subsequently by many others.† Originally platinized platinum was used for unattackable indicator electrodes, but later smooth electrodes of the same metal were employed; the potentials were measured against a standard half-cell. A simplification suggested by Hostetter and Roberts‡ was developed by Willard and Fenwick;§ this depends on the fact that not all inert electrodes show the same potential in an oxidation-reduction system. By choosing a suitable pair of metals, both of which are dipped in the titrated solution, the calomel electrode could be eliminated, since the difference in potential between the two metals undergoes a marked change at the end-point.¶ Willard and Fenwick** have used the polarized electrode system consisting of two similar or dissimilar electrodes for detecting the end-point of oxidation-reduction titrations; a modification known as the 'dead-stop' end-point method, which avoids the use of a potentiometer or voltmeter, was suggested by Foulk and Bawden.††

Electrometric Titration Apparatus—Although titration may generally be carried out in an open beaker it is sometimes convenient, or even necessary, to have special forms of apparatus; various types have been developed to suit different purposes.‡‡ In order to increase the accuracy of measurement of potential differences, or to make the titration process self-registering, application has been made of the amplifying properties of the thermionic valve.§§

* *Z. anorg. Chem.*, 1900, 24, 225.

† *Ann. Reports Chem. Soc.*, 1916, *et seq.*; Hildebrand, *loc. cit.* (p. 389); Kremann and Müller (R.), *op. cit.* (see p. 370), 1930, 732 *et seq.*; and review references cited on p. 388 *supra*.

‡ *J. Amer. Chem. Soc.*, 1919, 41, 1343 footnote.

§ *Ibid.*, 1922, 44, 2504; also van Name and Fenwick, *loc. cit.*

¶ For use of this bi-metallic electrode system, see Furman, *ibid.*, 1928, 50, 268, 273, 277; Wright and Gibson, *Ind. Eng. Chem.*, 1927, 19, 749; Lifschitz and Reggiani, *Gazzetta*, 1931, 61, 195.

** *J. Amer. Chem. Soc.*, 1922, 44, 2516; 1923, 45, 84, 928, 933; van Name and Fenwick, *loc. cit.*

†† *J. Amer. Chem. Soc.*, 1926, 48, 2045; Brann and Clapp, *ibid.*, 1929, 51, 39; Pring (M. E.) and Spencer (J. F.), *Analyst*, 1930, 55, 375.

‡‡ Hostetter and Roberts (H. S.), *loc. cit.*; Treadwell and Weiss, *Helv. Chim. Acta*, 1919, 2, 680; Garner and Waters, *J. Soc. Chem. Ind.*, 1922, 41, 337 T; Bovie, *J. Amer. Chem. Soc.*, 1922, 44, 2892; Spencer, *J. Soc. Chem. Ind.*, 1927, 46, 423 T; Morton, *Trans. Faraday Soc.*, 1928, 24, 14.

§§ Goode, *J. Amer. Chem. Soc.*, 1922, 44, 26; 1925, 47, 2483; Calhane and Cushing, *Ind. Eng. Chem.*, 1923, 15, 1118; Treadwell and Paoloni, *Helv. Chim. Acta*, 1925, 8, 89; Williams and Whitenack, *J. Physical Chem.*, 1927, 31, 519; Morton, *loc. cit.*; Callan and Horrobin, *J. Soc. Chem. Ind.*, 1928, 47, 329 T; Partridge, *J. Amer. Chem. Soc.*, 1929, 51, 1; Kassner *et al.*, *ibid.*, 1932, 54, 2278; Clarke (B. L.), *Ind. Eng. Chem. (Anal.)*, 1931, 3, 321; Garman and Drosz, *ibid.*, 1935, 7, 341; Willard and Hager, *ibid.*, 1936, 8, 341.

Modified Titration Methods—These modifications consist chiefly of devices for the detection of the end-point; * in addition it has been shown that the end-point of a titration may be calculated by observing the change of electrode potential, at any stage, resulting from the addition of a known amount of titrant.†

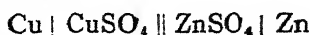
Equilibrium Constants and E.M.F.—According to the van 't Hoff isotherm the change of free energy in a reversible process is given by

$$-\Delta G = RT \ln K - RT \sum \nu \ln a \quad . \quad . \quad . \quad (\text{lix})$$

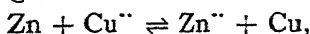
where a represents the activities of resultants and reactants, and K is the equilibrium constant. If the activities of all the reacting and resulting species are unity, then $-\Delta G = RT \ln K$. The E.M.F. of a reversible cell is a measure of the maximum work (free energy) resulting from the chemical or physical changes occurring in the cell, and $-\Delta G = nFE$; in the special case under consideration, therefore,

$$E = \frac{RT}{nF} \ln K \quad (\text{lx})$$

where n is the number of faradays passing for the completion of the reaction. In the cell



the reaction occurring is



and at equilibrium

$$K = \frac{a_{\text{Zn}^{++}}}{a_{\text{Cu}^{++}}} \quad . \quad . \quad . \quad (\text{lxii})$$

regarding the activities of the solid metals as constant. If E_0 is the E.M.F. of this cell when both zinc and copper ions are at unit activity, then

$$E_0 = \frac{RT}{2F} \ln K \quad . \quad . \quad . \quad (\text{lxiii})$$

With the ions at unit activity the metals exhibit their standard electrode potentials, and the E.M.F. of the cell may be written

$$E_0 = \frac{\pi_0}{\text{Cu}, \text{Cu}^{++}} - \frac{\pi_0}{\text{Zn}, \text{Zn}^{++}} = \frac{RT}{2F} \ln K \quad . \quad (\text{lxiii})$$

* Sand and Law, *J. Soc. Chem. Ind.*, 1911, 30, 3; Pinkhof, *Chem. Weekblad*, 1919, 16, 1163; Treadwell, *Helv. Chim. Acta*, 1919, 2, 672; Müller, *Die Elektrometrische Massanalyse*, 1923, p. 78; Cavanagh, *J. Chem. Soc.*, 1927, 2207.

† Cavanagh, *ibid.*, 1928, 843, 855; 1930, 1425; Fenwick, *Ind. Eng. Chem. (Anal.)*, 1932, 4, 144. For further references to this and other aspects of electrometric titration, see Glasstone, *loc. cit.* 1933 (p. 388 *supra*).

By means of this equation the equilibrium constant K of the reaction occurring in the cell may be determined from a knowledge of the standard electrode potentials. The same treatment is applicable to other cases of equilibria between two metals and their respective ions. In the case under discussion, π_0 and π_0 are



about 0.34 and -0.76 respectively; hence at ordinary temperatures K is roughly 10^{38} . Since the ionic activities are approximately proportional to their concentrations it follows that when the system is at equilibrium the ratio of zinc ion to copper ion concentration is extremely large. If zinc is put into contact with a solution of copper sulphate, therefore, the zinc will displace the copper ions from solution until it is almost exhausted of the latter, and $[\text{Zn}^{++}]/[\text{Cu}^{++}]$ is *circa* 10^{38} ; that is, zinc will replace copper completely, within the limits of analytical accuracy.

From a knowledge of normal electrode potentials it is thus possible to determine the extent to which one metal will replace another, or hydrogen,* from a solution of its ions; it appears that the greater the difference between the normal electrode potentials of two metals the more completely will the one with the more negative potential replace the other. If complex ions are formed, however, this will not hold; thus in the presence of an excess of potassium cyanide, copper can displace zinc from solution to a small extent. Both zinc and copper ions are removed in the form of complex cyanide ions, but since the cuprocyanide complex is the more stable the ratio $[\text{Zn}^{--}]/[\text{Cu}^{--}]$ may even exceed 10^{38} ; the copper will thus tend to dissolve and zinc to precipitate in order to restore equilibrium. Although copper should not displace hydrogen to any appreciable extent, it dissolves in hydrobromic acid and even in potassium cyanide solution with the evolution of hydrogen; in each case the copper ions are removed in the form of complex ions, and the actual electrode potential of copper may be more negative than that of hydrogen in the same solution. In general for two metals M_1 and M_2 ,

$$E_0 = \frac{\pi_0}{M_1, M_1^{++}} - \frac{\pi_0}{M_2, M_2^{++}} \quad \frac{RT}{nF} \ln K = \frac{RT}{nF} \ln \frac{a_{M_2^{++}}}{a_{M_1^{++}}} : \quad (\text{lxiv})$$

$$\text{hence} \quad \frac{\pi_0}{M_1, M_1^{++}} + \frac{RT}{nF} \ln a_{M_1^{++}} = \frac{\pi_0}{M_2, M_2^{++}} + \frac{RT}{nF} \ln a_{M_2^{++}} \quad (\text{lxv})$$

where $a_{M_1^{++}}$ and $a_{M_2^{++}}$ represent the *equilibrium* activities of the two ions. The two sides of this equation represent the electrode potentials of the two metals; hence in the equilibrium system the two metal potentials are equal. The metal with the more

* Allowance must be made for hydrogen overvoltage (see p. 420).

negative potential in contact with a given solution will, therefore, dissolve and displace the other until the two electrode potentials are the same; equilibrium is then established.

Since the equilibrium constant in a metal displacement reaction may be calculated from a knowledge of standard electrode potentials, information concerning the latter may be obtained if the equilibrium constant is known. This method has been used by Noyes and Toabe* to determine the electrode potential of tin; finely divided lead and tin were shaken with solutions containing lead and tin perchlorates until equilibrium was attained. By analysis it was found that $[\text{Sn}(\text{ClO}_4)_2]/[\text{Pb}(\text{ClO}_4)_2]$ was then 2.98 at 25°, and this may be regarded as equal to the equilibrium constant $a_{\text{Sn}^{2+}}/a_{\text{Pb}^{2+}}$, assuming ionization and activity coefficients to be the same for the two salts. Since π_0 is -0.122, then from equation (lxv)

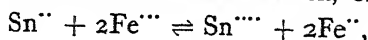
$$-0.122 - \pi_0 = 0.0295 \log 2.98$$

$$\text{Sn, Sn}^{2+}$$

$$\therefore \pi_0 = -0.136 \text{ volt.}$$

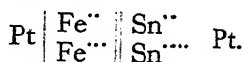
$$\text{Sn, Sn}^{2+}$$

For a reversible oxidation-reduction reaction, e.g.



$$\text{at equilibrium} \quad K = \frac{a_{\text{Sn}^{4+}} \times a_{\text{Fe}^{2+}}^2}{a_{\text{Sn}^{2+}} \times a_{\text{Fe}^{3+}}^2}; \quad (\text{lxvi})$$

this reaction occurs in the cell



When all the substances are at unit activity the two electrode potentials are the respective standard oxidation-reduction values, and their algebraic difference is the E.M.F. of the cell; thus

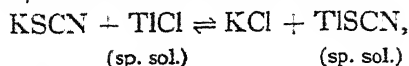
$$E_0 = \pi_0_{\text{Fe}^{3+}, \text{Fe}^{2+}} - \pi_0_{\text{Sn}^{4+}, \text{Sn}^{2+}} = \frac{RT}{2F} \ln K \quad (\text{lxvii})$$

Since $\pi_0_{\text{Fe}^{3+}, \text{Fe}^{2+}}$ is +0.77 and $\pi_0_{\text{Sn}^{4+}, \text{Sn}^{2+}}$ is -0.15, the equilibrium constant for the reaction between stannous and ferric ions may be evaluated as roughly 10^{80} . It is clear, therefore, that stannous ions reduce ferric ions almost completely; the deviation from 100 per cent. reduction could not be estimated analytically. It may be readily shown, as has been done for the zinc-copper system, that at equilibrium the separate electrode potentials become equal; and

* *J. Amer. Chem. Soc.*, 1917, **39**, 1537; see also Noyes and Brann, *ibid.*, 1912, **34**, 1016; Popoff *et al.*, *ibid.*, 1931, **53**, 1643; Schumb and Sweetser, *ibid.*, 1935, **57**, 871; Heymann and Jellinek, *Z. physikal. Chem.*, 1932, **160**, 34.

the *E.M.F.* of the cell with reactants and resultants at equilibrium concentrations, as is to be expected, is zero.*

Another type of equilibrium—one of the first to be studied by *E.M.F.* methods†—is involved in the reaction



occurring in the cell

Thallium amalgam	KCl solution saturated with TlCl	KSCN solution saturated with TlSCN	Thallium amalgam.
---------------------	--	--	----------------------

Since solid TlCl and TlSCN are present their activities may be taken as constant; hence at equilibrium

$$K = a_{\text{KCl}}/a_{\text{KSCN}} \approx [\text{KCl}]_e/[\text{KSCN}]_e \quad \text{. . . (lxviii)}$$

assuming the activity coefficients of the potassium salts to be approximately equal. Applying the van 't Hoff isotherm, it follows that

$$-\Delta G = nFE = RT \ln K - RT \ln [\text{KCl}]/[\text{KSCN}]. \quad \text{(lxix)}$$

where $[\text{KCl}]$ and $[\text{KSCN}]$ represent *arbitrary* concentrations of these salts, and n is equal to unity; hence

$$E = \frac{RT}{F} \ln K - \frac{RT}{F} \ln \frac{[\text{KCl}]}{[\text{KSCN}]} \quad \text{(lxx)}$$

From this expression it is possible either to determine the equilibrium constant of the reaction at various temperatures, if the *E.M.F.* of the cell is measured with solutions of known concentration, or alternatively the *E.M.F.* may be calculated if K is known. The latter can be evaluated by analysis of equilibrium solutions and the results so obtained are in good agreement with those deduced from *E.M.F.* measurements. These results provided the first confirmation of van 't Hoff's view that the *E.M.F.* of a cell could be regarded as a measure of the free energy change of the reaction occurring in it.

Complex Ions—The electrode potential method for determining the formulæ of relatively stable complex ions was first suggested by Bodländer‡ and applied§ to the study of complex cyanides.

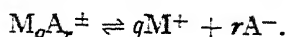
* See Smith, *Analytical Processes*, 1929, p. 195 *et seq.*, for examples of analytical importance; see also p. 395 *supra*.

† Knüpfner, *Z. physikal. Chem.*, 1898, 26, 255

‡ *Festschrift zu Dedekind*, 1901, p. 1109, see *Abs. Chem. Soc.*, 1902, ii, 63; Jacques, *Trans. Faraday Soc.*, 1910, 5, 225; also Jeffery, *ibid.*, 1922, 17, 709; 1924, 20, 390. For a graphical method applicable in certain cases, see Koch, *J. Chem. Soc.*, 1930, 2053; 1931, 1418.

§ Bodländer *et al.*, *Z. physikal. Chem.*, 1902, 39, 597; *Z. anorg. Chem.*, 1902, 31, 458; *ibid.*, 1904, 39, 197; *Ber.*, 1903, 36, 3945; Sherrill, *Z. physikal. Chem.*, 1903, 43, 705; Euler, *Ber.*, 1903, 36, 1854, 2878,

Suppose $M_qA_r^\pm$ is the formula of a complex ion, where M^+ and A^- are the positive and negative ions from which the complex is formed, and with which it is in equilibrium, thus:



If the law of mass action is applicable—using concentrations instead of activities since the method is approximate and the latter are not usually available—then

$$\frac{[M^+]^q [A^-]^r}{[M_qA_r^\pm]} = k \quad . \quad . \quad . \quad (lxxi)$$

Consider two solutions of different concentrations, at the same temperature, then

$$\frac{[M^+]_1^q}{[M^+]_2^q} = \frac{[M_qA_r^\pm]_1 [A^-]_2^r}{[M_qA_r^\pm]_2 [A^-]_1^r} \quad . \quad . \quad . \quad (lxxii)$$

Suppose a concentration cell is made up with electrodes of the metal M dipping in the two solutions under discussion, then the *E.M.F.*, E , will be given by

$$E = \frac{RT}{nF} \ln \frac{[M^+]_1}{[M^+]_2} = \frac{RT}{qnF} \ln \frac{[M_qA_r^\pm]_1 [A^-]_2^r}{[M_qA_r^\pm]_2 [A^-]_1^r} \quad (lxxiii)$$

(a) If the solutions both contain the same large proportion of a neutral salt of the anion A^- , then the small amount of this ion resulting from the dissociation of the complex may be neglected, and $[A^-]_1$ and $[A^-]_2$ may be regarded as equal. Under these conditions

$$E_a = \frac{RT}{qnF} \ln \frac{[M_qA_r^\pm]_1}{[M_qA_r^\pm]_2} \quad . \quad . \quad . \quad (lxxiv)$$

In a stable complex almost the whole of the metal M is present in the complex ion, hence

$$\frac{[M_qA_r^\pm]_1}{[M_qA_r^\pm]_2} = \frac{[\text{Total } M]_1}{[\text{Total } M]_2} \quad (lxxv)$$

$$q \approx \frac{RT}{nFE_a} \ln \frac{[\text{Total } M]_1}{[\text{Total } M]_2} \quad (lxxvi)$$

and q may be evaluated if the *E.M.F.* of the concentration cell is measured directly or determined from the separate electrode potentials.

(b) If the two solutions have the same concentration of com-

3400; Pick, *Z. anorg. Chem.*, 1906, 51, 1; Jeffery, *loc. cit.* The formation of internal complexes can be studied by an analogous method, see Riley *et al.*, *J. Chem. Soc.*, 1932, 514; 1934, 1440, 1448; 1936, 1121.

plex ion, or, if the ion is stable, the same total concentration of M, then

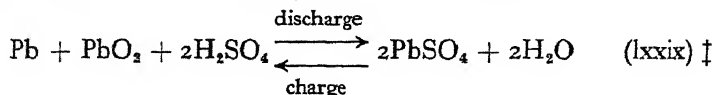
$$E_b \approx \frac{RT}{nF} \ln \frac{[A^-]_2^r}{[A^-]_1^r} \quad (\text{lxxvii})$$

$$\frac{RT}{nFE_b} \ln \frac{[A^-]_2}{[A^-]_1} \quad (\text{lxxviii})$$

Since q is known, r may be determined and hence the complete formula of the complex ion is obtained.

Accumulators or Secondary Cells—When an electric current is passed through an electrolytic cell chemical changes are produced and the electrical energy is transformed into chemical energy. If the cell is reversible then on removing the source of current and connecting the poles of the cell by a conductor, electrical energy will be produced at the expense of the stored chemical energy. Such a device may be regarded as an **accumulator**, or **storage battery**, for electrical energy; certain chemical changes occur when the accumulator is 'charged' with electricity, and these changes are reversed during discharge. Theoretically any reversible cell should be able to store electrical energy, but for practical purposes most cells are ruled out on the grounds of low electrical capacity, incomplete reversibility as to physical form of the substances involved, chemical action when idle, cost of materials, etc.* Only two types of accumulator have hitherto obtained any prominence; they are (a) the lead accumulator, consisting of an electrode of lead and one of lead dioxide immersed in sulphuric acid, and (b) the Edison, or alkaline, accumulator which has electrodes of iron and nickelic hydroxide in potassium hydroxide solution. The theoretical aspects only of these storage batteries will be considered here.

The Lead Accumulator—The chemical actions occurring in this cell were first made clear by Gladstone and Tribe in 1883; † the charged cell may be represented by $\text{PbO}_2 | \text{H}_2\text{SO}_4 | \text{Pb}$, and on discharge the positive pole is reduced and the negative oxidized to lead sulphate; on charging the reverse reaction occurs, thus



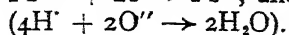
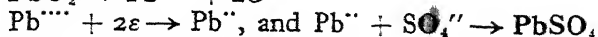
* For requirements of storage batteries and details of construction, etc., see Foerster, *Elektrochemie wässriger Lösungen*, 1922, p. 241; Allmand and Ellingham, *Applied Electrochemistry*, 1924, p. 235; Crennell and Lea, *Alkaline Accumulators*, 1928, p. 5; Vinal, *Storage Batteries*, 1930.

† *The Chemistry of Secondary Batteries*, 1883.

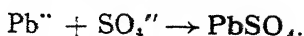
‡ An alternative theory, according to which the electromotively active substance at the positive electrode is supposed not to be PbO_2 , but a

The separate electrode processes during discharge of the accumulator may be written :

At Positive Electrode :



At Negative Electrode : $\text{Pb} \rightarrow \text{Pb}^{++} + 2\varepsilon$



The reverse process, involving the conversion of the sulphate into lead dioxide and lead respectively, occurs when the cell is charged. The potential of the positive electrode, π_1 , may be regarded as due to the oxidation-reduction system $\text{Pb}^{++++} + 2\varepsilon \rightleftharpoons \text{Pb}^{++}$, that is

$$\pi_1 = \frac{\pi_0}{\text{Pb}^{++}, \text{Pb}^{++++}} + \frac{RT}{2F} \ln \frac{[\text{Pb}^{++++}]}{[\text{Pb}^{++}]} \quad \quad (\text{Ixxx})$$

where $[\text{Pb}^{++++}]$ and $[\text{Pb}^{++}]$ are the concentrations of the respective ions; the ratio of these is assumed to be equal to the ratio of their activities. From the known solubilities of lead dioxide and of lead sulphate—these are the substances present at the positive electrode when the accumulator is producing current—in sulphuric acid solution,* it may be calculated that $[\text{Pb}^{++++}]$ and $[\text{Pb}^{++}]$ are equal to 0.91×10^{-4} and 5×10^{-6} gm. ion per litre respectively, in sulphuric acid of specific gravity 1.15 at 18° ;† since π_0 is $\text{Pb}^{++}, \text{Pb}^{++++}$

+ 1.74 volt at ordinary temperatures, it follows that

$$\begin{aligned} \pi_1 &= 1.74 + 0.029 \log (0.91 \times 10^{-4} / 5 \times 10^{-6}) \\ &= 1.80 \text{ volts.} \end{aligned}$$

At the negative electrode the potential π_2 is due to the system

higher oxide Pb_2O_5 or Pb_2O_7 , was suggested by Féry (*J. Physique*, 1916, 6, 21, 187; *Compt. rend.*, 1924, 179, 1153; 1925, 181, 606); this view, however, does not seem to be well substantiated, MacInnes, Adler and Joubert, *Trans. Amer. Electrochem. Soc.*, 1920, 37, 641; Knobel, *ibid.*, 1923, 43, 99; Jumau, *ibid.*, 1928, 53, 245; see also Mazza, *Atti R. Accad. Lincei*, 1926, 4, 215; 1927, 5, 688; Denina, *Chem. Abs. (U.S.A.)*, 1926, 20, 3135; 1928, 22, 2516; Lottermoser and Grützner, *Z. anorg. Chem.*, 1924, 140, 93; Riesenfeld and Sass, *Z. Elektrochem.*, 1933, 39, 219; Ishikawa, *Bull. Inst. Phys. Chem. Res. Japan*, 1934, 13, 1027; Harned and Hamer, *J. Amer. Chem. Soc.*, 1935, 57, 33, for various studies concerned with the mechanism of the lead accumulator. The E.M.F. of this accumulator rises rapidly from 2.2 to 2.7 volts when completely charged; the higher voltage may be due to the formation of traces of a higher oxide (see Glasstone, *J. Chem. Soc.*, 1922, 121, 1469, 2091).

* Cf. Cumming, *Trans. Faraday Soc.*, 1907, 2, 199; *Z. Elektrochem.*, 1907, 13, 19.

† Allmand and Ellingham, *op. cit.*, pp. 250-1.

Pb | Pb⁺⁺, where the concentration of plumbous ions is produced by the dissolution of lead sulphate in the acid; the value of [Pb⁺⁺] is then 5×10^{-6} gm. ion per litre as at the positive electrode. It follows that

$$\begin{aligned}\pi_2 &= \frac{RT}{2F} \ln [\text{Pb}^{++}] \quad \quad \quad (\text{lxvii}) \\ &= -0.12 + 0.029 \log (5 \times 10^{-6}) \\ &= -0.27 \text{ volt.}\end{aligned}$$

The *E.M.F.* of the accumulator as a whole is equal to $\pi_1 - \pi_2$, that is to 2.07 volts; the measured value 2.01 volts is in good agreement. Since the solubility of lead dioxide, and hence the value of [Pb⁺⁺⁺⁺], is proportional to the fourth power of the acid concentration, whereas the value of [Pb⁺⁺] is inversely proportional to the sulphate ion concentration (approximately),* it may be shown that the *E.M.F.* of the lead accumulator increases with increasing acid concentration.

Acid Concentration—Dolezalek † has been able to show the effect of acid concentration in another manner; when an accumulator is being charged 2 mols. of water are removed and 2 mols. of sulphuric acid are produced (equation lxxix), whereas in the discharge the acid is removed and the water formed. The acid solution therefore becomes more concentrated when the cell is charging, and more dilute on discharge. Suppose two accumulators, containing acid at different concentrations, are connected through a resistance with the two positive and the two negative electrodes together; the cell with the more concentrated acid will then charge the other in order that the acid concentrations may become equalized and equilibrium thus attained. Clearly, the accumulator containing the more concentrated acid must have the higher *E.M.F.* The passage of 2 faradays through the complete circuit will cause changes equivalent to the transfer of 2 gm. mols. of acid from the more concentrated to the more dilute solution, and of 2 gm. mols. of water in the opposite direction. The osmotic and mechanical work involved, which depends on the concentrations and vapour pressures of the solutions, may be equated to the electrical work $2F(E_1 - E_2)$, where E_1 and E_2 are the *E.M.F.*'s of the cells with more concentrated and dilute acid respectively. The calculations made by Dolezalek were found to be in good agreement with experimental observations; these results

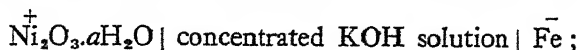
* $[\text{Pb}^{++++}][\text{O}']^2 = L_1$ (solubility product of lead dioxide); $[\text{H}]^2[\text{O}'] = k_1$ (ionic product of water); hence $[\text{Pb}^{++++}] = k_1[\text{H}]^4$. Also $[\text{Pb}^{++}][\text{SO}_4'] = L_2$ (solubility product of lead sulphate); hence $[\text{Pb}^{++}] = L_2/[\text{SO}_4']$.

† *Z. Elektrochem.*, 1899, 5, 538.

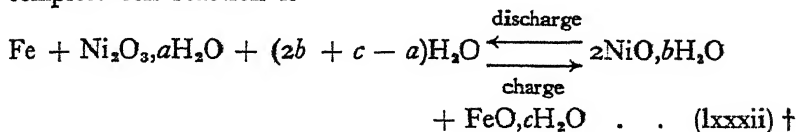
support the 'double sulphation' theory proposed by Gladstone and Tribe.

The heat evolved in the reaction occurring in the lead accumulator during discharge (equation lxxix) is known to be about 89,500 calories with an acid of specific gravity 1.15; this is a measure of the *total* energy change, whereas the *E.M.F.*, 2.01 volt, is proportional to the *free* energy change. Substituting these values in the appropriate form of the Gibbs-Helmholtz equation (p. 287), the temperature coefficient of the lead accumulator, dE/dT , may be calculated as + 0.00024 volt/degree; the measured value with acid of the given concentration is + 0.00026.* The agreement supplies further evidence for the interpretation given here of the source of *E.M.F.* of the lead accumulator.

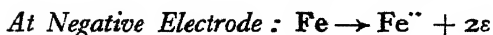
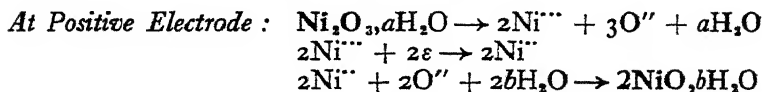
The Alkaline (Edison) Accumulator—The charged condition of this cell may be represented, in its simplest form, by :



on discharge the hydrated nickelic oxide is reduced to nickelous oxide, whereas the iron is oxidized to hydrated ferrous oxide. The complete cell reaction is



The actual reactions are probably much more complex, but the equation given represents the main process.† The separate electrode processes during discharge may be written as :



The positive electrode may thus be regarded as an oxidation-reduction system $\text{Ni}^{+++} + \varepsilon \rightarrow \text{Ni}^{++}$, and the negative potential as

* Thibaut, *ibid.*, 1913, 19, 881.

† The values of a , b and c are uncertain and indefinite, since the exact formulæ of the 'hydroxides' and the amounts of adsorbed water are unknown.

‡ Zedner, *Z. Elektrochem.*, 1905, 11, 809; 1906, 12, 463; 1907, 13, 572; Foerster, *ibid.*, 1907, 13, 414; 1908, 14, 285; 1910, 16, 461; Faust, *ibid.*, 1907, 13, 161. The fully charged cell probably contains some NiO_2 at the positive electrode.

due to the electrode $\text{Fe} | \text{Fe}^{++}$; the *E.M.F.* of the whole cell is therefore given by:

$$E = \frac{\pi_0}{\text{Ni}^{++}, \text{Ni}^{+++}} + \frac{RT}{F} \ln \frac{[\text{Ni}^{+++}]}{[\text{Ni}^{++}]} - \frac{\pi_0}{\text{Fe}, \text{Fe}^{++}} - \frac{RT}{2F} \ln [\text{Fe}^{++}]$$

$$= \frac{\pi_0}{\text{Ni}^{++}, \text{Ni}^{+++}} - \frac{\pi_0}{\text{Fe}, \text{Fe}^{++}} + \frac{RT}{2F} \ln \frac{[\text{Ni}^{+++}]^2}{[\text{Ni}^{++}]^2 [\text{Fe}^{++}]} \quad (\text{lxxxiii})$$

If the three oxides are considered as being present either in the anhydrous form, or as the simple hydroxides $\text{Ni}(\text{OH})_2$, $\text{Ni}(\text{OH})_3$, and $\text{Fe}(\text{OH})_2$, then from a consideration of the solubility products it may be shown that

$$[\text{Ni}^{+++}]^2/[\text{Ni}^{++}]^2 [\text{Fe}^{++}] \text{ is a constant,}$$

and the *E.M.F.* of the accumulator should be independent of the alkali concentration. In actual practice it is found that the value is 1.33 to 1.35 volts (positive electrode + 0.55, and negative - 0.8, approx.), and varies somewhat with the concentration of potassium hydroxide; the cause of this variation is the water adsorbed by the colloidal hydrated oxides, and the consequent changes in the value of $[\text{OH}^-]$. It has been found that the quantity $2b + c - a$ in equation (lxxxii) is positive, and water is removed during discharge of the accumulator; it may be shown, therefore, by the arguments applied in the case of the lead accumulator that the more concentrated the alkali the lower the *E.M.F.* of the cell. This is in agreement with the observations of Foerster.* A thermodynamic treatment, similar to that used by Dolezalek in a study of the lead accumulator, has been applied † and the effect of dilution of the alkali on the *E.M.F.* of the Edison storage battery has been accounted for quantitatively in terms of the vapour pressure of the solution.

Modified forms of the Edison accumulator, in which the iron is replaced by zinc and the alkali saturated with zinc hydroxide, as in the Drumm battery,‡ or by cadmium have attracted attention in recent years.§

* *Loc. cit.*, 1908.

† See Roeber, *Trans. Amer. Electrochem. Soc.*, 1902, 1, 195; Zedner, *loc. cit.*, 1906; Crennell and Lea, *op. cit.*, 95-8.

‡ See Allmand, *Nature*, 1932, 129, 386; cf. also, Michalowski, *D.R.P.*, 112351; Lasczynski, *Z. Elektrochem.*, 1901, 7, 821.

§ Grube and Doetsch, *ibid.*, 1936, 42, 247.

CHAPTER XVI

ELECTROLYTIC POLARIZATION

DECOMPOSITION Voltage—The subject of electrode potentials in the static or equilibrium condition has already been discussed, and a study must now be made of the changes which occur as a result of the passage of an electric current through a cell consisting of two electrodes dipping into an electrolyte.

If two small sheets of smooth platinum are immersed in dilute sulphuric acid and an external *E.M.F.* of about 1 volt applied

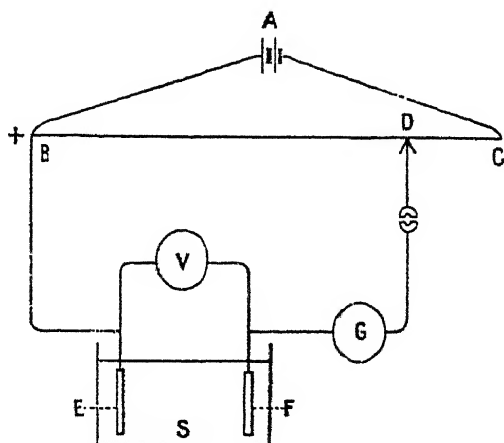


FIG. 28.—The measurement of decomposition voltage

from a battery, then a galvanometer, or other current strength indicator, placed in the circuit will at first show that an appreciable current is flowing; the strength, however, rapidly decreases to a very small value. On increasing the applied *E.M.F.* the magnitude of the current changes slowly until a point is reached at which the value suddenly increases; it will be observed, in general, that from this point onwards bubbles of gas are freely evolved from the electrodes. The experiment may be carried out by means of the apparatus shown diagrammatically in Fig. 28. A battery, *A*, is connected across a uniform resistance *BC*, along which can be moved a contact maker *D*; the fall of potential between *B* and *D*

can thus be varied gradually. Two smooth platinum electrodes, E and F , are placed in the cell S containing, say, N -sulphuric acid; G is a galvanometer, or milli-ammeter, and V is a high resistance voltmeter placed between the two electrodes, across the cell. The contact maker D is first brought close to B so that only a small $E.M.F.$ is applied to the electrodes E and F ; the fall of potential across the cell and the current flowing through it are read off on the instruments V and G respectively. The applied voltage is then increased in stages by moving D towards C , and the readings of the voltmeter and galvanometer noted after allowing a minute or two for the values to become steady. By plotting the applied voltage against the current strength a curve of the type

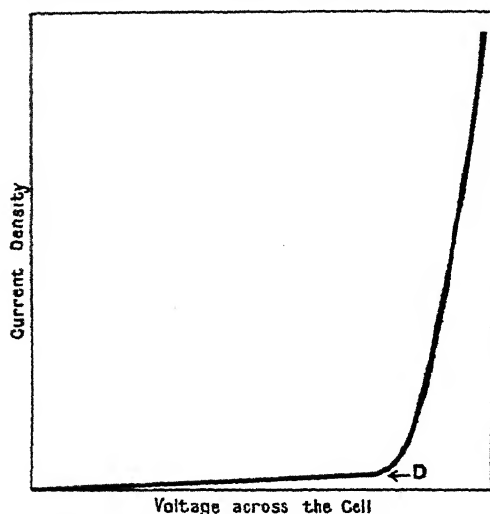


FIG. 29.—Decomposition voltage curve

shown in Fig. 29 is obtained; the sudden increase of current occurs at the point D , which represents in the case under consideration a fall of potential across the cell of about 1.7 volts.

On breaking the circuit it will be observed that the reading on the voltmeter V remains at first fairly steady and then decreases, more or less rapidly, to zero (Fig. 30). The cell S is evidently behaving as a source of current and its initial $E.M.F.$ is only slightly smaller than that previously applied by means of the battery A ; it is said to be exerting a **back $E.M.F.$** , since the latter acts in a direction *opposite* to that of the applied $E.M.F.$ This back $E.M.F.$ undoubtedly results from the accumulation of oxygen and hydrogen at the anode (E) and cathode (F) respectively. Two gas electrodes are thus produced, and the potential difference between them

opposes the applied *E.M.F.* If the primary current from *A* is shut off, then the cell *S* itself produces a fairly steady current until the oxygen and hydrogen gases accumulated at the electrodes are used up, or have diffused away; the voltage of the cell then falls to zero. This back *E.M.F.* must, of course, be operative even whilst current is being forced through the cell, and its existence in fact accounts for the shape of the curve in Fig. 29. When a small *E.M.F.* is first applied there is a sudden flow of current through the cell which causes the liberation of some hydrogen and oxygen at the electrodes; a back *E.M.F.* is thus rapidly set up and would almost completely oppose the flow of current if the gases could accumulate. As a result of diffusion these gases are slowly removed from the electrodes, and a very small current can pass through

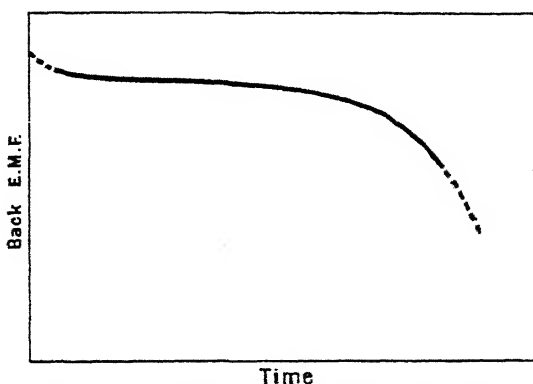


FIG. 30.—Change of back *E.M.F.* with time

the cell, only sufficient, however, to liberate enough oxygen and hydrogen to restore the amounts lost by diffusion. As the applied *E.M.F.* is increased the gases accumulate rapidly; but as their removal still only takes place by diffusion the current flowing through the cell remains small. A point is eventually reached, however, at which the accumulation of gas is so great that bubbles commence to form, and considerable quantities of oxygen and hydrogen can be readily removed in this way from the electrodes. Quite large currents can now pass through the cell without causing any appreciable increase in the accumulation of gases, and hence in the back *E.M.F.** Small increases in the applied *E.M.F.* beyond this critical condition will thus result in a rapid rise in the magnitude of the current able to flow through the circuit.

The point *D* (Fig. 29) at which the sudden increase of current

* The simple point of view considered here is not necessarily complete, as will be seen from the discussion of overvoltage in Chap. XVII.

occurs as the applied voltage is gradually raised, is called the decomposition point; in general, it is here that the evolution of both hydrogen and oxygen in the form of bubbles is first observed. The applied *E.M.F.* at the point *D* is called the **decomposition voltage** of the electrolyte; at this voltage the steady decomposition of the water of the electrolyte by means of the electric current commences, *without the aid of diffusion*.* At the decomposition point the accumulation of gases at the electrodes has almost reached a maximum; hence the back *E.M.F.* of the cell measured after a period of electrolysis is almost the same as at the decomposition point. Since the value is almost identical with the applied voltage at this point, the decomposition potential of a solution may be determined approximately by observing the constant back *E.M.F.* obtained from a cell after electrolysis has been proceeding freely for some time (see Fig. 30).

The small current which flows through the cell before the decomposition point is reached is called the **residual current**, and its value depends on the rate at which electromotively active material, in this case hydrogen and oxygen, can be removed from the electrodes by diffusion.† When the residual current is small, then the rise in the current-voltage curve at the decomposition point (Fig. 29) is very marked. By stirring the electrolyte, or by raising the temperature, it is possible to increase the rate of removal of the gases from the electrodes, and the strength of the residual current may be quite appreciably increased; although the actual value of the decomposition voltage is not altered by stirring, the break in the current-voltage curve, is, naturally, less pronounced.

The phenomena described in connection with the electrolysis of sulphuric acid solution with platinum electrodes are classed under the general title of **polarization**; this term is applied to all cases in which the flow of an electric current causes an electrode to be disturbed from its equilibrium, or static, condition. The electrodes disturbed in this way are said to be **polarized**; the battery *A* in Fig. 28 is called a **polarizing battery**, and the current flowing through the cell *S* is termed the **polarizing current**. The cur-

* The voltage (*E*) across the cell, measured by the voltmeter *V*, is made up of the difference of potential between the anode (ϵ_a) and the cathode (ϵ_c), and the fall of potential across the electrolyte; the latter term is obtained from Ohm's Law by multiplying the current flowing (*i* amp.) by the resistance of the cell (*r* ohms). Thus $E = \epsilon_a - \epsilon_c + ir$, and $\epsilon_a - \epsilon_c$, which at the point *D* represents the true decomposition voltage, is equal to $E - ir$; since *i* is very small under these conditions, and *r* not very large, the correction *ir* may be neglected and the voltage measured on *V* is taken as the true value.

† If the solution contains oxygen, as it will do unless anode and cathode compartments are separated and access of air is prevented, reaction with hydrogen at the cathode will increase the residual current.

rent produced when the polarized electrodes are short-circuited after the polarizing current is switched off is sometimes referred to as the **polarization current**.

Concentration Polarization—If a solution of copper sulphate is electrolyzed, using copper electrodes, it is found that as long as the current strength is small the *E.M.F.* which must be applied across the cell is in accordance with the requirements of Ohm's Law, i.e. it is equal to the product of the current in amperes and the resistance in ohms. Under these conditions the electrodes in the cell are exerting no back *E.M.F.*, and so are not polarized. For appreciable currents, however, the applied *E.M.F.* exceeds the value obtained from the application of Ohm's Law, and the difference increases with increasing current strength; the cell is now producing a back *E.M.F.* and the electrodes have become polarized. This change is brought about by the dissolution of the copper anode resulting in an increase of the cupric ion concentration in its vicinity, whilst the discharge of these ions at the cathode results in a decrease of concentration there; hence a concentration cell is produced the *E.M.F.* of which opposes the applied *E.M.F.* With very small currents diffusion prevents any appreciable concentration changes in the neighbourhood of the electrodes, but with larger currents polarization, i.e. a disturbance of the equilibrium condition, ensues. This particular type of polarization is called **concentration polarization**; it can be diminished by increasing the rate of diffusion of the electrolyte, e.g. by stirring the solution, by increasing its concentration, and by raising the temperature, but it cannot be entirely eliminated. It is very probable from observations on concentration polarization, and from other experiments during electrolysis, that there is always immediately adjacent to the electrode a thin layer of solution the concentration of which differs from that of the bulk of the electrolyte. This layer is called the **diffusion layer**, and its apparent thickness depends on those factors which influence the rate of diffusion.*

* For various studies concerned with properties of the diffusion layer, see Salomon, *Z. physikal. Chem.*, 1897, 27, 54; Sand, *ibid.*, 1900, 35, 461; *Phil. Mag.*, 1901, 1, 45; *Trans. Faraday Soc.*, 1905, 1, 1; Cottrell, *Z. physikal. Chem.*, 1903, 42, 385; Brunner, *ibid.*, 1904, 47, 56; Nernst and Merriam, *ibid.*, 1905, 53, 235; Milner, *Phil. Mag.*, 1905, 9, 645; Roseburgh and Miller, *J. Physical Chem.*, 1910, 14, 816; Redman, *ibid.*, 1925, 29, 1548; Burt-Gerrans, *ibid.*, 1926, 30, 396; Verschaffelt, *Rec. trav. chim.*, 1922, 41, 764; 1923, 42, 332; 1924, 43, 125; Aten, *ibid.*, 1923, 42, 337; Procopiu, *Compt. rend.*, 1917, 164, 725; Wilson and Youtz, *Ind. Eng. Chem.*, 1923, 15, 603; Glasstone, *J. Chem. Soc.*, 1925, 127, 1824; Müller and Konopicky, *Z. Elektrochem.*, 1928, 34, 840; Eucken, *ibid.*, 1932, 38, 341; Butler and Armstrong, *Proc. Roy. Soc.*, 1933, 139 A, 406; Samarcov, *Z. physikal. Chem.*, 1934, 168, 45; see also, Glasstone and Hickling, *Electrolytic Oxidation and Reduction*, 1935, Chap. III.

As a general rule the magnitude of the concentration polarization is quite small; according to the equation for the *E.M.F.* of a concentration cell a ten-fold change of ionic concentration will only result in a change of 0.029 and 0.058 volt for bi-valent and uni-valent ions respectively. In some cases, however, as a result of special circumstances the concentration polarization voltage may be much larger. For example, if a solution of sodium argentocyanide, made by saturating sodium cyanide solution with silver cyanide, is electrolyzed between silver electrodes an *E.M.F.* of polarization up to about 1 volt may be observed; this is entirely due to concentration changes. In this particular instance it has been found that a small alteration in the ratio of silver to free cyanide ions in the solution causes a marked change in the electrode potential, as a consequence of the nature of the complex argentocyanide ion.* A small change in the silver concentration resulting from dissolution at the anode and deposition at the cathode then produces marked changes of electrode potential. The magnitude of the polarization voltage is, therefore, quite large, although the actual extent of polarization is small.

Abnormal Concentration Polarization—There is another type of concentration polarization which is possible. In the electrolysis of a solution containing a metal in the form of a complex ion, the latter must dissociate into its simple constituents before deposition of the metal can occur on the cathode. Consider, for example, a metal *M* which forms a simple cyanide MCN and a complex anion $M(CN)_2'$; the equilibrium $M(CN)_2' \rightleftharpoons M' + 2CN'$ then exists in the solution. The M' ions are discharged at the cathode and they can only be replaced by subsequent decomposition of the complex ion, since the above equilibrium is displaced. If this restoration of equilibrium occurs rapidly then the concentration of M' ions will be maintained, but if the process is a slow one there may be a deficiency resulting in an indirect type of concentration polarization. Since the concentration of M' ions in a complex cyanide solution is generally very minute, the changes which occur will be relatively large and considerable polarization may result. It was considered at one time that the polarization observed in the electrolysis of cuprocyanide solutions was of this type, due to the slowness of the dissociation of cuprocyanide into cuprous ions: $Cu(CN)_2' \rightarrow Cu' + 2CN'$,† but this view is probably incorrect.‡ It is possible, however, that other cases may exist in which the dissociation of a complex ion is slow; in these circumstances stirring the electrolyte should have little effect on the polarization,

* Glasstone, *J. Chem. Soc.*, 1929, 690.

† Foerster, *Z. Elektrochem.*, 1907, 13, 561.

‡ Glasstone, *J. Chem. Soc.*, 1929, 702.

although an increase of temperature should increase the rate of dissociation and so reduce polarization.

Depolarization—Concentration polarization of the simple type is observed when a Daniell cell produces current, as well as when a current is passed through it. In the former case the zinc, i.e. negative, electrode dissolves and the concentration of zinc ions in its vicinity increases and causes the electrode to become *less* negative; at the positive copper electrode cupric ions are discharged, so their concentration will decrease and the electrode becomes *less* positive. The Daniell cell is, therefore, liable to concentration polarization whilst working, and its *E.M.F.* as a result becomes smaller. The polarization may be prevented by using saturated solutions of zinc and copper sulphates containing crystals of the respective salts; the concentration changes are thus reduced to a minimum, and the *E.M.F.* of the cell remains almost constant when supplying current. One of the oldest examples of polarization of a cell acting as a source of electricity was that observed in the simple element consisting of two different metal plates, e.g. zinc and copper, dipping in dilute acid. When first set up a fairly large current may be drawn from such a cell, but the magnitude soon decreases to a small value. The production of current is associated with the liberation of hydrogen at the positive, i.e. copper, electrode, with the result that this begins to act like a hydrogen electrode with a less positive potential (see Table XLV, p. 331). The total *E.M.F.* of the cell is thus reduced from about 1.1 volts to 0.6 volt, the polarization being due to the accumulation of hydrogen at the positive electrode. If an oxidizing agent is added to the electrolyte the hydrogen can be removed as fast as it is formed and hence its accumulation is prevented; the potential of the positive electrode is thus not appreciably reduced, polarization does not occur, and the cell maintains its *E.M.F.* whilst supplying current. Any substance which reduces polarization, in this particular case an oxidizing agent, is called a **depolarizer**. In primary cells various solid, liquid and gaseous depolarizers have been employed to prevent the fall in *E.M.F.* (see p. 507). Depolarizers may also be used to reduce the polarization resulting from the passage of current through a cell when hydrogen and oxygen gases are liberated; the cathodic depolarizer should be an oxidizing agent, and the anodic depolarizer a reducing agent. This depolarization is of practical importance in connection with the preparation of organic compounds by electrolytic oxidation and reduction processes (see Chap. XX). Polarization due to the evolution of chlorine may be reduced by the addition of a substance capable of ready chlorination.

The solid mercurous chloride in a calomel half-element is often called a depolarizer; it prevents any appreciable alteration of the

mercurous ion concentration in the vicinity of the mercury electrode resulting from the accidental passage through, or withdrawal of, an excessive current from the cell during *E.M.F.* measurements. Any solids present for the purpose of maintaining a constant concentration of ions, e.g. mercurous sulphate in the $\text{Hg} | \text{Hg}_2\text{SO}_4(\text{s}) | \text{H}_2\text{SO}_4$ half-element, or in the Weston cell (p. 286), or even the copper and zinc sulphates in the Daniell cell, may be called depolarizers, because they prevent disturbance of the electrode equilibrium.

Results of Decomposition Voltage Measurements—Although a large number of observations of polarization effects had already been made,* the work of Le Blanc† marked the commencement of a new era in which many confusing phenomena have been correlated. Le Blanc first determined the decomposition voltages of a number of *N*-aqueous solutions of acids and alkalis; smooth platinum electrodes were used and an experimental method similar to that already described (p. 407). The results obtained are given in Table LVI.

TABLE LVI

DECOMPOSITION VOLTAGES OF *N*-SOLUTIONS BETWEEN SMOOTH PLATINUM ELECTRODES

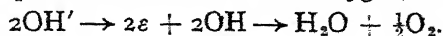
Solution.	Volts.	Solution.	Volts.
Sulphuric acid . .	1.67	Potassium hydroxide . .	1.67
Nitric acid . .	1.69	Ammonium hydroxide . .	1.74
Phosphoric acid . .	1.70	Methylammonium hydroxide	
Dichloroacetic acid	1.66	(<i>N</i> /4)	1.75
Malonic acid . .	1.69	Diethylammonium hydroxide	
Perchloric acid . .	1.65	(<i>N</i> /2)	1.68
Tartaric acid . .	1.62	Tetramethylammonium hy-	
Sodium hydroxide	1.69	droxide (<i>N</i> /8)	1.74

Since the decomposition potentials of these solutions are all in the vicinity of 1.7 volts, it was concluded that the same electrolytic process occurred at the electrodes in every case; the only process which could be common to all these aqueous solutions is apparently the discharge of hydrogen and hydroxyl ions, at the cathode and anode respectively, with the resultant liberation of hydrogen and oxygen. It appears, therefore, that although the current is actually *conducted* by all the kinds of ions present in the electrolyte, at the electrodes only those processes which take place most readily can occur. In the electrolysis of an acid solution almost the whole of the current is carried to the anode by the anions of the acid, e.g. SO_4^{--} in sulphuric acid. At the electrode, however, the discharge of hydroxyl ions, in spite of their very small concentration (about 10^{-14} gm. ions per litre), can apparently take place at a lower

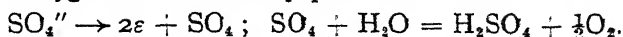
* See Roszkowski, *Z. physikal. Chem.*, 1894, 15, 267, for references.

† *Ibid.*, 1891, 8, 299; 1893, 12, 333.

potential than that of the anions of the acid. In all the solutions examined, therefore, it is probable that the hydroxyl ions give up their electrons at the anode, and form unstable hydroxyl radicals which react in pairs to form water and oxygen, thus :



At the cathode hydrogen ion discharge occurs, since this is the only cation present in the acid solution. The net electrolytic process is, therefore, the *primary* decomposition of water, as this ionizes to replace the discharged ions. It was considered at one time that the anions, e.g. SO_4^{2-} , were actually discharged at the anode, and the resulting free radicals then reacted with water to produce oxygen as a secondary product :



This view is probably incorrect, otherwise the decomposition voltage of an acid might be expected to depend on its nature ; the actual results (Table LVI) indicate that this is not the case.*

In the electrolysis of a solution of an alkali the current is carried to the cathode by the cations, e.g. Na^+ and NH_4^+ , but hydrogen ion discharge is almost certainly the process which can occur most readily in every case.† At the anode hydroxyl ion discharge occurs, as these are the only anions present ; electrolysis then again results in the primary decomposition of water, and not in the discharge of alkali metal ions and the secondary decomposition of water by the resulting metal. The decomposition voltage is thus almost independent of the nature of the alkali, and is the same as that for an acid where the primary process is identical.

With aqueous solutions of certain acids, particularly the halogen hydrides, the decomposition potentials are found to be below 1.7 volts, as shown by the results in Table LVII.

TABLE LVII

DECOMPOSITION VOLTAGES OF *N*-SOLUTIONS OF HALOGEN ACIDS

Hydrochloric acid	1.31 volts.
Hydrobromic acid	0.94
Hydriodic acid	0.52

Under these conditions, however, *halogen and not oxygen* is liberated at the anode, since the discharge of the halogen ions can occur more readily than that of hydroxyl ions ; the primary electrolytic process is now the decomposition of the halogen acid. On con-

* For a general discussion, see Glasstone, *School Science Review*, 1935, 328.

† See also Verschaefelt, *Natuurw. Tijdsch.*, 1926, 8, 121; *Chem. Abs. (U.S.A.)*, 1927, 21, 1585 ; at a mercury cathode the behaviour is exceptional, see p. 455.

tinued electrolysis, especially with dilute solutions, the decomposition voltage rises and the gas evolved then contains a large proportion of oxygen (see p. 498); the electrolytic process is once more the decomposition of water at about 1.7 volts.

Decomposition of Salt Solutions—The decomposition potentials of solutions of the sulphates and nitrates of alkali and alkaline earth metals were found by Le Blanc to be about 2.2 volts; this result suggests that the discharge of hydrogen and hydroxyl ions does not represent the primary electrode process. It must be remembered, however, that when working with neutral salts the removal of hydrogen and hydroxyl ions from the vicinity of the cathode and anode respectively, will cause the solution to become locally alkaline near the former electrode and acid near the latter (see p. 12). At the decomposition point, therefore, hydrogen ions are discharged from an alkaline solution, and hydroxyl ions from an acid solution. For salts of strong acids and strong bases the degree of alkalinity and acidity at the two electrodes will be almost constant; hence all such salts should have the same decomposition voltage. The results quoted in Table LVIII are from the work of Le Blanc.

TABLE LVIII

DECOMPOSITION VOLTAGES OF SALTS OF STRONG ACIDS AND BASES

Sodium nitrate . . .	2.15 volts.	Calcium nitrate . . .	2.11 volts.
Potassium nitrate . . .	2.17 "	Barium nitrate . . .	2.25 "
Lithium nitrate . . .	2.11 "	Sodium sulphate . . .	2.21 "
Strontium nitrate . . .	2.28 "	Potassium sulphate . . .	2.20 "

If the acidic or basic function of the salt is weak the decomposition voltage will generally be smaller, because the changes in the vicinity of the electrodes are less marked on account of buffer action. The decomposition potentials of alkali halide solutions, as with the free acids, is lower than for other salts. On continued electrolysis, however, halogen ion discharge is accompanied by hydroxyl ion discharge and the evolution of oxygen commences at about 2.2 volts.

Discharge Potentials at Separate Electrodes—In order to throw light on the problem of the discharge of ions Le Blanc* modified his apparatus so that the potential difference between each electrode and the electrolyte could be measured, as well as the difference of potential between the two electrodes. A standard half-element *G*, e.g. a calomel electrode, was introduced into the apparatus represented in Fig. 31, and by means of a tube *T*, and an intermediate vessel *V* containing electrolyte, the standard electrode could be connected with either of the test electrodes under observation, e.g. with the cathode *F*. The *E.M.F.* of the com-

* *Z. physikal. Chem.*, 1893, 12, 333.

bination of standard half-element and of the cathode, for example, of the electrolytic cell could be measured by means of a potentiometer, and so the potential of the test electrode calculated. In this way the discharge or **deposition potential** at each electrode * could be determined at the decomposition point of the electrolyte. With this experimental method Le Blanc found that in general the discharge potential of an ion, e.g. cadmium, silver and zinc ions, was equal to the static, or equilibrium, potential exhibited by the solid metal in the same solution. Thus, the potential of the cathode at the decomposition point of *N*-cadmium sulphate solution was -0.42 volt (on the hydrogen scale), whereas the ordinary reversible, or static, potential between metallic cadmium and the same solution is also -0.42 volt. This conclusion was confirmed by Bose †

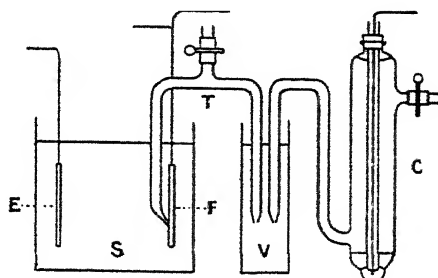
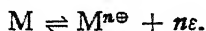


FIG. 31.—The measurement of single polarized electrode potentials

using a different experimental method. The tendency of a metal to go into solution as simple ions, as measured by its static potential, is therefore equal to the reluctance of the ions to give up their charges, as measured by the deposition potential. The process of ionization and discharge of a metal ion may, in general, be regarded as strictly reversible, thus



There are a few exceptions to this strict reversibility to which reference will be made later (p. 452).‡ Since the potential difference between a metal and a solution of its ions is more negative the less concentrated the solution, the deposition potential will also be more negative in a dilute than in a concentrated solution. Hence when large currents are passed through a solution, and the rapid dis-

* Strictly speaking this is the potential *difference* between the electrode and the electrolyte; the term 'electrode potential' is an abbreviated expression (see p. 293).

† *Z. Elektrochem.*, 1899, 5, 155.

‡ Iron, nickel and cobalt particularly show a considerable irreversibility.

charge of ions at the cathode results in a decrease of concentration in its vicinity, the potential becomes more negative; this concentration polarization at high rates of deposition leads to an *apparent* irreversibility.

The deposition potential of a metal is independent of the nature of the cathode material,* provided the deposited metal does not form an alloy with it; if this should occur the 'solution pressure', and hence equilibrium potential, of the metal is altered and a less negative potential is required to bring about deposition. This phenomenon is called 'depolarization of metal deposition'; it may also be observed when two metals capable of forming an alloy with one another are deposited simultaneously from a mixed solution (p. 460). The deposition of a metal does not depend on the nature of the anions, provided complex ion formation does not occur; the anodic and cathodic processes are thus independent. Exactly the same considerations with regard to ion discharge and deposition apply to the anode as have been discussed for the cathode. At the former electrode either negative ions, e.g. OH' , Cl' , may be discharged, or the metal of the electrode, e.g. copper, zinc, may itself give up electrons and dissolve to form positive ions. The condition for negative ion discharge is the same as for cations; the anode potential must be equal to the reversible potential for the resulting substance; thus the reversible potential of iodine in *N*-hydriodic acid solution is $+0.52$ volt, and the discharge, or deposition, potential of iodine in the same solution is 0.54 volt. The dissolution of a metal generally occurs when the anode potential is made slightly more positive than the reversible value in the particular solution used.

The decomposition voltage of an electrolyte is equal to the algebraic difference of the potentials of the two separate electrodes; when the decomposition point is reached *both* electrodes have attained their deposition potentials, and the free discharge of ions can occur at both anode and cathode. This condition is not necessarily reached simultaneously at the two electrodes, since the value of the current at which steady decomposition occurs depends on a number of factors, e.g. the nature of the deposited substance, its solubility in the electrode and electrolyte, and its power of reacting chemically with other substances present in solution. In any case a current-electrode potential curve, similar to the current-voltage curve (Fig. 29), may be plotted for each electrode; the discharge

* A certain thickness of deposit—very small in amount—seems to be necessary before this is strictly true; Oberbeck, *Ann. Physik*, 1887, **31**, 337; see also, Tödt, *Z. Elektrochem.*, 1928, **34**, 591; Bowden and Rideal, *Proc. Roy. Soc.*, 1928, **120 A**, 59; Nichols, *J. Amer. Chem. Soc.*, 1935, **57**, 267.

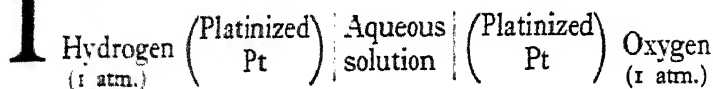
potential of the ion is then determined from the point on the curve at which there is a rapid increase of current for a small change of electrode potential.

If a number of processes are possible at an electrode they will take place in turn as the potential reaches the appropriate value. When the external *E.M.F.* applied to an electrolytic cell is increased the single potential of the cathode gradually becomes more negative, and that of the anode more positive. In an acid solution of copper sulphate the discharge potential of cupric ions, being equal to the static potential, is about $+ 0.34$ volt, whereas that of hydrogen ions is about $- 0.1$ volt ; hence on electrolysis the discharge of copper ions, and the deposition of copper on the cathode, will occur in preference to the liberation of hydrogen. When the copper is almost completely deposited then on increasing the voltage applied to the cell, so that the cathode potential can take on a more negative value, hydrogen evolution will commence. At a copper anode in the same electrolyte either dissolution of the metal, to form cupric ions, may occur at a potential of $+ 0.34$ volt, or discharge of hydroxyl ions at about $+ 1.1$ volt. Clearly the dissolution of the copper anode will occur in preference to the evolution of oxygen. If the anode were of platinum, which does not dissolve at all readily, the discharge of hydroxyl ions with the evolution of oxygen would be the first anodic process to occur.

CHAPTER XVII

OVERVOLTAGE

IT has been shown that the *E.M.F.* of the cell



should be about 1.2 volts, but is actually more nearly 1.10; hence the decomposition voltage of *any aqueous solution* from which the products are hydrogen and oxygen should be 1.1 – 1.2 volts, if the electrodes are reversible. With platinized platinum electrodes this is roughly the case at small current intensities, but with smooth platinum electrodes the decomposition voltage is about 1.70; the electrode material, therefore, introduces an irreversibility, or polarization effect. This polarization, which varies with the nature of electrode material, is of a type only observed when gases are liberated at an electrode; it was first studied systematically by Caspari* for the evolution of hydrogen. The potentials at which hydrogen bubbles commenced to be liberated from various cathodes in dilute sulphuric acid were determined, and the values compared with the potential of a reversible hydrogen electrode in the same solution. Only in the case of a platinized platinum cathode did gas bubbles appear at almost the reversible hydrogen potential; for all other metals an *excess* negative potential was required. The difference between the actual potential at which visible gas evolution *commenced* and the thermodynamically reversible value was called the *overvoltage*;† some of the overvoltage values determined by Caspari are given in Table LIX. In order to cause hydrogen bubbles to be evolved from a mercury cathode in 2*N*-sulphuric acid (reversible hydrogen potential *circa* 0.0 volt), a potential of – 0.78 volt must be applied, whereas at a copper cathode – 0.23 volt will suffice.

* Caspari, *Z. physikal. Chem.*, 1899, 30, 89; for earlier observations see Pirani, *Ann. Physik*, 1884, 21, 68; Le Blanc, *Z. physikal. Chem.*, 1891, 8, 299.

† The original German word was 'Überspannung'; it is sometimes translated 'supertension', or 'overpotential'.

TABLE LIX
OVERVOLTAGES IN *N*-SULPHURIC ACID SOLUTION

Platinized platinum	0.005 volt	Copper .	0.23 volt.
Gold	0.02	Cadmium	0.48
Iron (in NaOH) .	0.08	Tin .	0.53
Polished platinum	0.09	Lead .	0.64
Silver	0.15	Zinc .	0.70
Nickel	0.21	Mercury	0.78

The concept of overvoltage was extended by Tafel ; * this author measured the difference between the potential of an electrode at which hydrogen was being evolved by electrolysis at a definite *current density* (*C.D.*),† and that of a reversible hydrogen electrode in the same solution. The values obtained in this way are frequently called the overvoltages of the metals, although strictly speaking the term as originally used referred to the excess potential required before bubble evolution *commenced* ; in order to distinguish the two terms the latter is sometimes called the **minimum overvoltage**. The apparatus used by Tafel was of a type similar to that used in the determination of deposition potentials (Fig. 31) ; the potential difference between a standard electrode and the test cathode at which hydrogen was being liberated in a given electrolyte was measured by means of a potentiometer. These observations were made at a series of *C.D.*'s, the values of the latter being determined by dividing the strength of the current flowing through the circuit by the exposed area of the cathode. The reversible potential of the hydrogen electrode in the same solution was determined by means of a separate experiment, and so the overvoltage of the cathode at a series of *C.D.*'s could be calculated. Many observations of overvoltages have been made since the work of Caspari and of Tafel, and the methods of measurement have been somewhat modified ; it will be convenient to discuss these methods under two headings.

Measurement of Minimum Overvoltage—As a general rule although not invariably, the point at which bubbles commence to be evolved at an electrode coincides with that at which current begins to flow freely ; this also corresponds with the sudden rise—the 'break-point'—in the current-potential curve for the electrode. Certain authors ‡ prefer to use the determination of the break-point as a method for measuring the minimum overvoltage, since there is frequently a 'lag' in the formation of bubbles and the observation method may give results which are too high. In actual practice,

* *Ibid.*, 1905, 50, 641.

† Current density, written *C.D.*, is defined as current per unit area of electrode surface ; it is generally expressed as amps. or milliamps. per sq. cm. or per sq. dm.

‡ E.g. Coehn and Dannenberg, *Z. physikal. Chem.*, 1901, 38, 609.

however, the current-potential curves do not always show a definite break-point; * further, it has been emphasized by Westhaver † that as the curves are logarithmic, even for small currents, the apparent break-point depends on the relation between the scales used for current and potential. A better method would be to plot the potential against the *logarithm* of the current, and find the break-point in the resulting curve, but even this is not always satisfactory. ‡ Möller § extrapolated to zero current the current-potential curve obtained beyond the decomposition point, assuming the curve to be a straight line. The potential so obtained was regarded as the decomposition value corresponding with the true minimum overvoltage; this method is open to objection as the curve assumed to be a straight line was probably logarithmic. Thiel and Breuning, Glasstone || and Onoda ** have decided in favour of the method in which the evolution of bubbles is observed visually, provided that precautions are taken to prevent supersaturation of the electrode with gas. A fairly large current is applied to the electrode, preferably one with a roughened surface, so that bubbles of gas are evolved freely; the current is then reduced gradually until after waiting ten minutes for the electrode to reach a steady state not more than one gas bubble is evolved in the subsequent two minutes. The electrode potential is then measured and from it the minimum overvoltage is determined by subtracting the value for the reversible potential in the same electrolyte.

Measurement of Overvoltage at Definite Current-Density

—The method used by Tafel (p. 421) is called the 'direct' method; the results so obtained are liable to error because the potential of the electrode is being measured whilst the polarizing current is flowing through the circuit. If there is any appreciable resistance between the tip of the tube connecting the standard to the test electrode (*T*, Fig. 31) and the point at which the electrode is connected to the potentiometer system, a fall of potential equal (in volts) to the product of the resistance (in ohms) and the current (in amps.) will be included in the measured potential of the test electrode. †† This error should, if possible, be eliminated; at the suggestion of Luggin, ‡‡ Haber drew out into a capillary the

* See Wiedburg, *ibid.*, 1894, 14, 175; Gockel, *ibid.*, 1900, 32, 607; Thiel and Breuning, *Z. anorg. Chem.*, 1913, 83, 329.

† *Z. physikal. Chem.*, 1905, 51, 65.

‡ See Glasstone, *J. Chem. Soc.*, 1924, 125, 2414; Rideal and Bowden, *Proc. Roy. Soc.*, 1928, 120 A, 59.

§ *Z. physikal. Chem.*, 1908, 65, 226.

|| *loc. cit.*

** *Z. anorg. Chem.*, 1927, 162, 57; 1927, 165, 93.

†† See Glasstone, *J. Chem. Soc.*, 1923, 123, 2926.

‡‡ *Z. physikal. Chem.*, 1900, 32, 208.

tip of the connecting tube (*T*, Fig. 31), and fixed the end close to the surface of the polarized electrode in order to diminish the fall of potential due to the resistance of the electrolyte. Knobel, Caplan and Eiseman* have experimented with jets of different sizes for the end of the connecting tube; they concluded that the diameter should not be more than 1 mm. and that the tip should press 'directly but lightly against the electrode'. It is sometimes considered, however, that an error, much more serious than that due to the resistance of the electrolyte, is not eliminated in this way; this error is supposed to be due to the presence of a so-called 'transfer resistance' at the electrode surface, which is said to offer a mechanical opposition to the transfer of ions from electrolyte to electrode.† At low *C.D.*'s the resistance was thought to be equivalent to several thousands of ohms,‡ but this view has been modified.§ The possible error due to transfer resistance, if it exists, can only be obviated by measuring the electrode potential, or more strictly its contribution towards the back *E.M.F.*, when the polarizing current is switched off, so that the extraneous potential, equal to the product of current and resistance, is zero. In order to achieve this end Newbery and others|| have used a rotating commutator which in alternate half-revolutions connects the test electrode to the polarizing circuit and to the potentiometer system respectively.** The back *E.M.F.*, or potential of the electrode, is measured almost instantaneously after the polarizing current is switched off; by increasing the speed of rotation of the commutator to about 3,000 revs. per minute it was claimed that the measured potential was the true value from which the overvoltage should be determined. This potential is, however, the *average* during a period of 0.01 sec. after the polarizing circuit is broken; †† it may be quite different from that at the *instant* of switching off, since it has been found that the potential of an electrode falls very rapidly after the polarizing current ceases to flow,‡‡ especially if the electrolyte contains dissolved oxygen. The ordinary commutator method is thus of doubtful

* *Trans. Amer. Electrochem. Soc.*, 1923, 43, 55.

† Gore, *Proc. Roy. Soc.*, 1885, 38, 209; *Phil. Mag.*, 1886, 21, 130; Sand and Black, *Z. physikal. Chem.*, 1909, 70, 496; Newbery, *J. Chem. Soc.*, 1914, 105, 2422.

‡ Newbery, *Trans. Faraday Soc.*, 1919, 15, 126.

§ *Proc. Roy. Soc.*, 1925, 107 A, 486; 1926, 111 A, 182.

|| Newbery, *J. Chem. Soc.*, 1914, 105, 2422; 1916, 109, 1051, 1066; 1922, 121, 7; Sand *et al.*, *ibid.*, 1923, 123, 456.

** Le Blanc, *Z. physikal. Chem.*, 1890, 5, 469, used a vibrating tuning-fork for a similar purpose.

†† See Glasstone, *J. Chem. Soc.*, 1924, 125, 250.

‡‡ Dunnill, *ibid.*, 1921, 119, 108; Glasstone, *loc. cit.*; Knobel, *J. Amer. Chem. Soc.*, 1924, 46, 2613; Sand, Lloyd and Grant, *J. Chem. Soc.*, 1927, 378.

value, and conclusions concerning transfer resistance drawn from results obtained by this method are not satisfactory. In recent years there has been an accumulation of opinion against the existence of any mechanical opposition to the transfer of ions,* and the idea of transfer resistance is being discarded or modified.

It is possible, however, that there may be a resistance of a few ohms at the surface of a polarized electrode owing to the presence of gas and of a thin layer of electrolyte in immediate contact with the electrode—the diffusion layer (p. 411)—which cannot be eliminated by pressing the tip of the 'Luggin capillary' as close as possible to the test electrode. The resistance of this electrode-gas-electrolyte system has been called the 'surface resistance' † and the error to which it gives rise should, if possible, be eliminated in overvoltage measurement. Glasstone ‡ has devised a method which allows this to be done and yet gives a reasonably accurate value for the electrode potential; by means of a special commutator the almost instantaneous potential of the polarized electrode is measured at 0.002, 0.004, 0.006 and 0.012 sec. after the circuit is broken, and the results so obtained are extrapolated to give the value at zero time, i.e. at the instant of switching off the current. This is regarded as the true electrode potential, and is independent of resistance errors. Provided the electrolyte is sufficiently concentrated, e.g. more than about $N/2$, the potential obtained by the 'commutator-extrapolation' method is found to be equal to that measured by the 'direct' method, if the polarizing current is less than about 0.01 amp. If larger currents are used the differences between the results obtained by the two methods increase; these differences are presumably due to the surface resistance, and the value of the latter has been estimated to be of the order of one or two ohms for a N -solution of strong acid or alkali. An increase of temperature causes the surface resistance to decrease, whereas dilution of the electrolyte results in an increase; both these factors influence the resistance of the film of electrolyte included in the surface system. At very low current values, e.g. when bubble evolution commences, the surface resistance error is very small, and hence the minimum overvoltage may be measured by the direct method; in fact this is the only method available at present, since with such small currents the electrode potential does not reach its equilibrium value

* See MacInnes, *J. Amer. Chem. Soc.*, 1920, 42, 2233; Dunnill, *loc. cit.*; Tartar and Keyes, *J. Amer. Chem. Soc.*, 1922, 44, 557; Tainton, *Trans. Amer. Electrochem. Soc.*, 1922, 41, 389; Ferguson *et al.*, *ibid.*, 1924, 45, 311; 1925, 47, 227; 1933, 64, 221; *J. Physical Chem.*, 1932, 36, 1156, 1166, 2437; 1934, 38, 1117; 1935, 39, 191; Bowden, *Proc. Roy. Soc.*, 1930, 126 A, 107; for review, see Denina, *Gazzetta*, 1934, 64, 527.

† Glasstone, *J. Chem. Soc.*, 1923, 123, 2926.

‡ *Ibid.*, 1924, 125, 250; *Trans. Faraday Soc.*, 1924, 19, 808.

because of the repeated 'make and break' of the circuit by the commutator.

With some electrodes the rate of fall of potential after the polarizing circuit is broken may be so great that accurate extrapolation to zero time is not possible; in such cases the instantaneous value measured about 0.005 sec. after the current is switched off will give a comparative idea of the overvoltage.* The general slope of the potential-time curve may be determined by utilizing the observation that for currents less than 0.01 amp. in *N*-solutions there is very little error in the electrode potential determined by the direct method; an approximate extrapolation, at least, may then be carried out for larger values of the polarizing current. In recent years a number of studies of hydrogen overvoltage have been made in solutions completely free from dissolved oxygen, and often saturated with hydrogen. The residual current under these conditions, and the rate of depolarization, is small, so that appreciable overvoltages may be attained with quite low currents, especially if relatively small electrodes are used. The resistance errors under these conditions are quite negligible.†

Results of Hydrogen Overvoltage Measurements ‡— Although the results of many investigations on overvoltage are to be found in the literature of electrochemistry, there is no satisfactory agreement between them; this is not only due to the uncertainty concerning the method of measurement, but it is also connected with the influence of various physical factors not easy to control. It is definitely established that the nature of the electrode surface affects both the minimum overvoltage and that measured at a definite *C.D.*,§ and with continued use as a cathode the surface of many metals is considerably changed.|| It is to be expected, therefore, that overvoltage should alter with the duration of polarization; in general there is a decrease with increasing time, although at the commencement of polarization an increase may occur.** Clearly, overvoltage results cannot be very definite, and general tendencies only may be observed and discussed.

* Sand, Grant and Lloyd, *loc. cit.*

† Cf. Bowden and Rideal, *loc. cit.*

‡ A discussion of oxygen overvoltage will be deferred until other anodic properties of electrodes have been described.

§ See Roszkowski, *Z. physikal. Chem.*, 1894, 15, 287; Müller, *Z. anorg. Chem.*, 1900, 26, 1; Strasser and Gahl, *Z. Elektrochem.*, 1901, 7, 11; Glasstone, *J. Chem. Soc.*, 1924, 125, 2412.

|| Newbery, *ibid.*, 1914, 105, 2422; Rideal, *J. Amer. Chem. Soc.*, 1920, 42, 94.

** Roszkowski, *loc. cit.*; Müller (E.) and Weber, *Z. Elektrochem.*, 1903, 9, 958; Newbery, *J. Chem. Soc.*, 1916, 109, 1052; Harkins and Adams (H. S.), *J. Physical Chem.*, 1925, 29, 205.

Minimum Hydrogen Overvoltage—The minimum overvoltage at an electrode depends on its previous treatment, and it has been stated that the most reproducible results are obtained if the metal is first made an anode before being used as a cathode. The potential at which visible gas evolution commences is lower at a roughened than at a smooth surface of the same metal; thus the minimum overvoltage at a platinized platinum cathode is about 0.09 volt below that at a smooth electrode (Table LIX). The only systematic investigation of a large number of metal cathodes was made by Thiel,* but roughened surfaces were used and the results are much lower than those of Caspari (Table LIX). Other factors must, however, be operative, since for mercury, which apparently has a constant surface, Caspari obtained an overvoltage of 0.78, whereas Thiel and Hammerschmidt record 0.57 volt. In Tables LX and LXA are given some of the results obtained by Thiel *et al.*; the observations were made under uniform conditions and hence are comparable, but they are probably lower than the values for an average electrode.

TABLE LX

MINIMUM OVERVOLTAGES AT ROUGHENED CATHODES IN 2*N*-H₂SO₄ AT 25°

Cathode.	Volt.	Cathode.	Volt.	Cathode.	Volt.
Palladium .	0.000	Vanadium .	0.135	Graphite .	0.355
Platinum .	0.000	Nickel . .	0.137	Arsenic .	0.369
Ruthenium .	0.0004	Tungsten .	0.157	Bismuth .	0.388
Osmium . .	0.0015	Molybdenum .	0.168	Tantalum .	0.39
Iridium . .	0.0025	Copper . .	0.19	Lead . .	0.40
Rhodium .	0.004	Tin . . .	0.19	Indium .	0.53
Gold . . .	0.0165	Antimony .	0.233	Mercury .	0.57
Silver . . .	0.097				

TABLE LXA

MINIMUM OVERVOLTAGES IN VARIOUS ELECTROLYTES AT 25° (METALS ATTACKED BY 2*N*-SULPHURIC ACID)

Cathode.	Volt.
Cobalt . .	0.067 in <i>N</i> /100 - H ₂ SO ₄
Iron . . .	0.175 „ <i>N</i> /10 - H ₂ SO ₄ or FeSO ₄
Iron . . .	0.08 „ <i>N</i> - NaOH
Chromium .	0.18 „ <i>M</i> /100 - Cr(C ₂ H ₃ O ₂) ₃
Titanium .	0.24 „ <i>N</i> /10 - H ₂ SO ₄
Aluminium	0.296 „ <i>N</i> /100 - H ₂ SO ₄ or HCl
Manganese	0.37 „ <i>M</i> /10 - Mn(C ₂ H ₃ O ₂) ₂
Thorium .	0.38 „ <i>M</i> /20 - Th(C ₂ H ₃ O ₂) ₄
Cadmium .	0.39 „ <i>N</i> /100 - H ₂ SO ₄
Tin . . .	0.40 „ <i>N</i> /100 - H ₂ SO ₄
Zinc . . .	0.48 „ <i>M</i> /100 - Zn(C ₂ H ₃ O ₂) ₂
Thallium .	0.57 „ <i>N</i> /100 - H ₂ SO ₄

* Thiel and Breuning, *loc. cit.*; Thiel and Hammerschmidt, *Z. anorg. Chem.*, 1923, 132, 15.

The influence of temperature on minimum overvoltage has not been studied to any great extent, but it is generally accepted that overvoltage decreases with increasing temperature. Möller* found that the overvoltage at a mercury cathode in *N*/10-sulphuric acid reached a maximum value at 5.3° ; at this temperature the angle of contact between mercury and a bubble of hydrogen in the acid is also a maximum. Since the angle depends on the tensions at the various interfaces, Möller concluded that the minimum overvoltage is dependent on surface forces. According to Thiel and Breuning powerful bathotonic substances, e.g. butyric acid and amyl alcohol, which lower surface tension very considerably, actually raise the overvoltage at a platinum cathode; this is apparently the reverse of the effect to be expected from Möller's work. It has pointed out, however, that these bathotonic substances will be appreciably adsorbed and so alter the nature of the electrode-gas-electrolyte interfaces.†

Glasstone‡ found that ethyl and methyl alcohols, and acetic acid, substances which decrease the surface tension of water moderately, cause a definite lowering of the minimum overvoltage at a lead cathode; thus in an aqueous *N*-sulphuric acid solution (surface tension, 73 dynes per cm.) the overvoltage is 0.61, but in similar solutions containing 70 per cent. by weight of ethyl alcohol, 76 per cent. of methyl alcohol, or 80 per cent. of acetic acid, the overvoltages are 0.46, 0.43 and 0.45 respectively, whereas the surface tensions are 28, 29 and 36 dynes per cm. If the solution contained a strongly bathotonic substance, e.g. iso-butyl alcohol, or iso-amyl alcohol, the overvoltage appeared first to increase and then to decrease with increasing concentration of the added substance. An attempt was made by Onoda§ to correlate the minimum overvoltage of a mercury cathode in various solutions of acids containing salts with the interfacial tension between mercury and the solution; it was found that the overvoltage generally increased as the interfacial tension increased. No relationship could, however, be found between the overvoltage and the surface tension at the hydrogen-electrolyte interface.

The minimum overvoltage of a cathode appears to be independent of the hydrogen ion concentration of the electrolyte over wide limits, e.g. from pH 0 to pH 12; this has been found for lead, mercury, nickel, copper, and platinized and smooth platinum

* *Z. physikal. Chem.*, 1909, 65, 626; *Ann. Physik*, 1908, 25, 725.

† MacInnes and Adler, *J. Amer. Chem. Soc.*, 1919, 41, 194.

‡ *Trans. Faraday Soc.*, 1925, 21, 36; see also, Carrara, *Z. physikal. Chem.*, 1909, 69, 75.

§ *Z. anorg. Chem.*, 1927, 165, 93.

electrodes.* In alkaline solutions, however, the minimum overvoltage is often slightly less than in acid solutions.

There has been a tendency for some authors to ignore, or even to deny, the possibility that the so-called minimum overvoltage has a theoretical significance.† When working with solutions saturated with hydrogen, bubbles of gas are evolved at extremely low *C.D.*'s and in such electrolytes the point of minimum overvoltage may not only be very difficult to observe, but it may also be of little interest. In the presence of depolarizers, however, as for example in electrolytic reduction (see Chap. XX), the *C.D.* at which gas bubbles commence to be evolved is of considerable importance. There is good reason for believing that the value of the minimum overvoltage is independent of the presence of depolarizers, provided they do not affect the interfacial tensions, and it does not apparently vary with the nature of the gas, e.g. hydrogen, oxygen or nitrogen, saturating the electrolyte. It is also not appreciably influenced by changes of hydrogen ion concentration, over a considerable range, as already noted, or by the application of high-frequency oscillations.‡ These results would seem to establish the minimum overvoltage as a definite property of an electrode, but even if the theoretical significance is open to question there is no doubt as to its practical importance.

Overvoltage at Appreciable *C.D.*'s—For a given *C.D.* the overvoltage should be independent of the actual area of the cathode, and this may serve as a test of the reliability of the method for measuring overvoltage.§ Several authors have deduced theoretically || that overvoltage increases logarithmically with increasing *C.D.* according to the formula

$$\omega = a + b \log I, \quad (i)$$

where ω is the overvoltage, a and b are constants, and I is the *C.D.* These deductions are all based on a general assumption that the overvoltage is proportional to the logarithm of the concentration of an electromotively active material; this concentration will be a function of the current strength, and so the formula given may be readily derived. A more accurate form is

$$\omega = a + b \log (I - c), \quad (ii)$$

* Glasstone, *J. Chem. Soc.*, 1924, 125, 2414, 2646; *Analyst*, 1925, 50, 327; Meunier, *J. Chim. phys.*, 1925, 22, 629.

† See, for example, Baars, *Sitzungsber. Ges. Beförd. Naturw. Marburg*, 1928, 63, 213; Baars and Kayser, *Z. Elektrochem.*, 1930, 36, 429.

‡ Glasstone and Reynolds, *Trans. Faraday Soc.*, 1932, 28, 582.

§ Glasstone, *ibid.*, 1924, 19, 808.

|| E.g. Jahn, *Z. physikal. Chem.*, 1898, 26, 385; Tafel, *ibid.*, 1905, 50, 641; Lewis and Jackson, *ibid.*, 1906, 56, 207; Westrip, *J. Chem. Soc.*, 1924, 125, 1112.

where c is a constant which allows for the removal of active material from the electrode by diffusion, etc.; * c becomes negligible at high $C.D.$'s or in the absence of a depolarizer, e.g. dissolved oxygen. Overvoltage measurements made by the direct and commutator-extrapolation methods appear to be in agreement with these formulæ; † an illustration is afforded by the results quoted in Table LXI.

TABLE LXI

VARIATION OF OVERVOLTAGE OF A LEAD CATHODE IN $N-H_2SO_4$ WITH CURRENT-DENSITY

[Calculated results from formula :— $\omega = 0.59 + 0.115 \log (I - 16.5)$.]

Overvoltage.			Overvoltage.		
$C.D. (I).$	Observed.	Calcd.	$C.D. (I).$	Observed	Calcd.
18 . . .	0.60	0.61	90 . . .	0.82	0.80
20 . . .	0.645	0.65	150 . . .	0.84	0.83
30 . . .	0.725	0.72	300 . . .	0.86	0.875
50 . . .	0.78	0.765	600 . . .	0.88	0.905

The value of b in equation (i) has acquired considerable importance in connection with theories of overvoltage: for a number of metals it has a value of 0.11 to 0.12 at ordinary temperatures, e.g. silver, gold, copper, mercury and nickel.† At platinum and palladium cathodes, however, b may be as low as 0.05,§ and at lead, in N -acetic acid, and tantalum, in sulphuric acid, it may be greater than 0.2.||

The fact that overvoltage depends on $C.D.$ accounts, to some extent, for the influence of the state of the electrode surface. A roughened electrode will have a much larger surface area than a smooth electrode of the same size; hence the *actual* $C.D.$, and the overvoltage, will be lower in the former case. Other factors, such as those causing a decrease of the minimum overvoltage, which are independent of $C.D.$ must, however, also be operative. Foerster** quotes some results for the influence of the condition of the elec-

* Glasstone, *ibid.*, 1924, 125, 2414; see also Bennewitz, *Z. physikal. Chem.*, 1910, 72, 202; Hammett, *J. Amer. Chem. Soc.*, 1924, 46, 7; Essin, *Z. physikal. Chem.*, 1933, 166, 270.

† Glasstone, *loc. cit.*; Knobel, Caplan and Eiseman, *loc. cit.*; Lattey, *Trans. Faraday Soc.*, 1924, 19, 829; Harkins and Adams, *loc. cit.*; Rideal and Bowden, *loc. cit.*; Müller (W. J.) and Konopicky, *Z. Elektrochem.*, 1928, 34, 840; measurements made by the original commutator method (e.g. Newbery, *J. Chem. Soc.*, 1916, 109, 1051) suggest that overvoltage is almost independent of $C.D.$, but the results are not reliable.

‡ Baars, *loc. cit.*; Bowden and Rideal, *loc. cit.*

§ Volmer and Wick, *Z. physikal. Chem.*, 1935, 172, 429; Knorr and Schwartz (E.), *ibid.*, 1936, 176, 161.

|| Erdey-Grúz and Wick, *ibid.*, 1932, 162, 53.

** *Elektrochemie wässriger Lösungen*, 1922, p. 311.

trode surface on the overvoltage of cadmium; these are given in Table LXII.

TABLE LXII
INFLUENCE OF SURFACE CONDITION ON OVERVOLTAGE OF CADMIUM
C.D.

Surface.	0.01 amp./cm. ²	0.0024 amp./cm. ²
Polished, silver-bright .	1.05 volt.	0.74 volt.
Smooth, matt-white .	0.96 "	0.68 "
Rough, grey .	0.67 "	0.59 "

The influence of temperature on overvoltage has not been investigated very fully, but it is definitely known that an increase of temperature causes a decrease of overvoltage; the published results are often unreliable on account of changes in the electrode surface during the course of measurement.* Thus Rideal† found the temperature coefficient of overvoltage of zinc in *N*/10-sulphuric acid to be -0.31 millivolt per degree, whereas from the measurements of Westrip‡ in *N*-sulphuric acid a value of -1.6 millivolt/degree is obtained. The most reliable results are those of Knobel and Joy, but as the overvoltages were measured by the direct method the temperature coefficients may contain an error resulting from variations in the surface resistance; the values obtained at low C.D.'s are probably the most accurate, and these are given in Table LXIII.

TABLE LXIII
TEMPERATURE COEFFICIENT OF OVERVOLTAGE IN ACID SOLUTION

Cathode Metal.	Coefficient in Millivolts/degree.
Platinized platinum	Nil
Lead . . .	- 1.6
Silver . . .	- 2.5
Nickel . . .	- 2.6
Copper	- 3.1

Bircher and Harkins§ state that a number of metals in *N*/10-sulphuric acid have a temperature coefficient of -2 millivolts/degree; this certainly appears to be so, for mercury,|| and a value of -2.2 millivolts/degree was obtained by Rideal** for copper. As a general working rule it is convenient, for most electrodes, to assume that the overvoltage decreases about 0.02 volt for every 10°

* Knobel and Joy, *Trans. Amer. Electrochem. Soc.*, 1923, **44**, 443.

† *J. Amer. Chem. Soc.*, 1920, **42**, 94.

‡ *Loc. cit.*

§ *Ibid.*, 1923, **45**, 2897.

|| Harkins and Adams, *loc. cit.*; Glasstone, *J. Chem. Soc.*, 1924, 125, 2651.

** *Loc. cit.*

the temperature is raised. It has been suggested by Bowden* (see p. 440) that the temperature coefficient of overvoltage is really a function of both overvoltage and the temperature at which it is measured; he has deduced an equation of the form

$$\frac{d\omega}{dT} = - \frac{\omega - 0.5\omega}{0.5T} \quad (\text{iii})$$

where $d\omega/dT$ is the temperature coefficient and ω is a constant for each cathode material. For mercury, ω has a value of about 0.77, and since the overvoltage is approximately 1 volt at appreciable *C.D.*'s the temperature coefficient is approximately - 2 millivolts/degree, according to equation (iii), at ordinary temperatures. For low overvoltage metals ω is smaller and so also is ω : hence $d\omega/dT$ remains almost constant for different metals, as found experimentally.

For some time the effect of pressure on overvoltage was uncertain, but Bircher and Harkins† and Knobel‡ concluded that hydrogen overvoltage is independent of the external pressure: more recently evidence has been obtained which suggests that there is a slight decrease of overvoltage, about 0.04 volt for 10 atms., as a result of an increase of pressure.§

The addition of colloidal substances, e.g. gelatine or gum arabic, to the electrolyte causes a lowering of surface tension but an increase of overvoltage.|| Pring and Tainton observed that the hydrogen bubbles were smaller than in the absence of colloidal material; this is probably accounted for by changes at the interfaces, which also affect the overvoltage. Ethyl and methyl alcohols lower the overvoltage at appreciable *C.D.*'s just as they do the minimum value. The presence of small amounts of impurities in the electrolyte may also influence the overvoltage.** In glacial acetic acid solutions hydrogen overvoltages are said to be greater than in aqueous electrolytes, in spite of the lower surface tension; the conditions, however, may be quite different in the former case.††

The variation of overvoltage at a definite *C.D.* with changes in the hydrogen ion concentration is difficult to determine, since

* *Loc. cit.*; see also Kobosev and Nekrassov, *Z. Elektrochem.*, 1930, 36, 529.

† *Loc. cit.* ‡ *J. Amer. Chem. Soc.*, 1924, 46, 2751.

§ Cassel and Krumbein, *Z. physikal. Chem.*, 1935, 171, 70; cf. also, Tammann and Jenckel, *Z. anorg. Chem.*, 1928, 173, 337; Schischkin *et al.*, *Z. Elektrochem.*, 1934, 40, 713, 724; 1936, 42, 631, 693.

|| Marie, *Compt. rend.*, 1908, 147, 1400; Pring and Tainton, *J. Chem. Soc.*, 1914, 105, 710; Isgarischev and Berkmann, *Z. Elektrochem.*, 1922, 28, 47; Westrip, *loc. cit.*

** Tafel, *loc. cit.*; Westrip, *loc. cit.*; Bowden, *Trans. Faraday Soc.*, 1927, 23, 571.

†† Swann and Edelmann, *Trans. Amer. Electrochem. Soc.*, 1930, 58, 75.

in order to obtain solutions of low acidity it is generally necessary to have present the salt of an alkali metal to conduct the current. At high *C.D.*'s alkali metal-hydrogen alloys may be deposited, or the alkali metal may form alloys with the cathode; in any case there will be an accumulation of alkali metal ions in the neighbourhood of the cathode. The electrode potentials obtained under these conditions are not necessarily comparable with those measured in a solution containing no positive ions other than hydrogen ions. Further, unless the solution is extremely well buffered, the rapid discharge of hydrogen ions at appreciable *C.D.*'s will decrease the acidity of the diffusion layer as a result of concentration polarization. As far as can be estimated, within the narrow limits permitted by the use of sulphuric acid solutions containing no added salts, the overvoltage at lead, mercury and antimony cathodes is independent of the hydrogen-ion concentration even at fairly large *C.D.*'s.* Herasymenko† working with a dropping mercury cathode (see p. 469) concluded, however, that the overvoltage increased steadily with decreasing concentration of hydrogen ions, every ten-fold decrease of concentration resulting in an increase of overvoltage of about 0.058 volt. The subject has been re-examined by Bowden,‡ who found that at low *C.D.*'s the overvoltage at a mercury cathode was almost independent of the pH of the electrolyte, but at higher *C.D.*'s the value increased with increasing pH; this change was attributed to concentration polarization at high *C.D.*'s.§ It is probable, therefore, that overvoltage is independent, to a great extent, of the hydrogen ion concentration of the solution in which it is determined.

It has been stated that electric waves and alternating currents decrease the hydrogen overvoltage at many metals; || the effect, at least as far as high-frequency oscillations are concerned, is not fundamentally on the overvoltage, but on the residual current, so that at a given *C.D.* the overvoltage is *apparently* lower. It is only so, however, because the *effective* polarizing *C.D.* is less when the high-frequency currents are passing.**

* Glasstone, *J. Chem. Soc.*, 1924, 125, 2414, 2646; Sand, Lloyd and Grant, *loc. cit.*; Lloyd, *Trans. Faraday Soc.*, 1929, 25, 525.

† *Rec. trav. chim.*, 1925, 44, 503; *Z. physikal. Chem.*, 1930, 149, 123. The conditions at a dropping cathode may not be comparable with those at a stationary one (see p. 471 *infra*).

‡ *Trans. Faraday Soc.*, 1928, 24, 473.

§ See also Lloyd, *ibid.*, 1930, 26, 12.

|| Rothmund and Lessing, *Ann. Physik*, 1904, 15, 193; Bancroft, *Trans. Amer. Electrochem. Soc.*, 1916, 29, 309; Glasstone, *J. Amer. Chem. Soc.*, 1925, 47, 940; Harkins and Adams, *loc. cit.*; Halla, *Z. Elektrochem.*, 1929, 35, 838.

** Glasstone and Reynolds, *loc. cit.*; see also, *idem*, *Trans. Faraday Soc.*, 1933, 29, 399.

Rate of Attainment of Overvoltage—A study of the rate at which an electrode acquires its overvoltage potential has led to results of some importance. It has been found that when working with an electrolyte saturated with hydrogen the rate of increase of potential is constant; the potential is a linear function of the quantity of electricity passed.* Only when the steady final potential is approached is there any indication of the rate falling off from its constant value. This result implies that during the early stages of the acquisition of the cathode potential, the whole of the current passed goes to charge up a double layer consisting of electrons, or negative ions, on the electrode side and of hydrogen ions on the side of the solution. The measured cathode potential at any instant is the actual potential across this double layer. The linear variation of the potential with the quantity of electricity indicates that the double layer acts virtually as a condenser, and its capacity is given by the slope of the curve, that is by $dQ/d\tau$, when the potential (τ) is plotted against the quantity of electricity (Q). From the work of Bowden and Rideal it appears that this capacity is 6×10^{-6} coulombs per volt per sq. cm. at a mercury cathode,† and it is probably the same for hydrogen evolution at all other electrodes, irrespective of the material, provided allowance is made for the true surface area. For example, the apparent capacity of the double layer on a bright platinum electrode is 13×10^{-6} , but on one of platinized platinum it is $11,000 \times 10^{-6}$ coulombs: it appears that in the former case the actual area of the electrode is about twice, and in the latter, about two thousand times, as great as the apparent area. This idea has been used as the basis of a method for comparing the available areas of various metals.‡

Since it is known that 6×10^{-6} coulombs per sq. cm. is required to raise the potential of a mercury cathode by one volt, the corresponding number of hydrogen atoms (or ions) present on the surface can be evaluated, remembering that 96,500 coulombs are required to discharge 1 gm. ion of hydrogen, which contains 6.06×10^{23} individual ions: the actual number calculated in this way is 3.7×10^{13} for one volt increase of potential. If the diameter of a mercury atom is 3×10^{-8} cms. then there will be about 10^{15} atoms per sq. cm., and if each of these is capable of holding

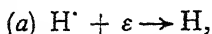
* Bowden and Rideal, *loc. cit.*; Baars, *loc. cit.*; Erdey-Grúz and Volmer, *Z. physikal. Chem.*, 1930, 150, 203.

† Proskurnin and Frumkin (*Trans. Faraday Soc.*, 1935, 31, 110), using a different method, find this capacity to be $18 - 20 \times 10^{-6}$ coulombs, and attribute lower values to traces of impurity on the electrode surface; see also Volmer and Wick, *Z. physikal. Chem.*, 1935, 172, 429.

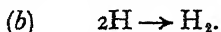
‡ Bowden and Rideal, *Proc. Roy. Soc.*, 1928, 120 A, 80; Bowden and Connor, *ibid.*, 1930, 128 A, 317.

one hydrogen atom, then only about one twenty-seventh part of the surface is covered for a rise of potential of one volt. It is clear, therefore, that minute amounts of material are sufficient to establish even high overvoltages. Experiments on the rate of self-discharge of a cathode in the absence of a depolarizer, after the polarizing current is cut off, suggests that the active material on the cathode may be little more than that requisite for setting up the double-layer potential considered above.*

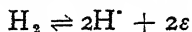
Theories of Overvoltage—Although the phenomena of overvoltage have been carefully studied there is no agreement as to their cause, or concerning the mechanism of hydrogen evolution; many theories have been proposed, and the more important will be reviewed briefly. The evolution of hydrogen at a cathode probably takes place in two stages, namely the discharge of the ion † to form atomic hydrogen



followed by the combination of the atoms to yield molecules, thus



If either of these stages occurs slowly then the process



will not be thermodynamically reversible and the evolution of hydrogen cannot take place at the reversible potential. Any retardation of the discharge of hydrogen ions to form molecules would, therefore, result in polarization and would lead to the necessity for an excess potential, i.e. overvoltage, to be applied to the electrode before gas evolution commenced.‡ The main theories of overvoltage may be divided roughly into two categories according as they postulate the first or second stage in the formation of molecules from ions to be the slow one.

If the actual discharge of the hydrogen ion, that is the union with an electron, is instantaneous, but the combination of the atoms to form molecules is not, then atomic hydrogen will accumulate in the cathode and the potential will become more negative than the reversible value.§ At one atmosphere pressure atomic hydrogen

* Armstrong and Butler, *Trans. Faraday Soc.*, 1933, 29, 1261.

† As already seen (p. 179) the hydrogen ion is probably H_3O^+ , although for convenience it is written here as H^+ simply.

‡ The term 'gas evolution' as used here applies to the gas at 1 atm. pressure. Strictly speaking hydrogen can be evolved at potentials below the overvoltage value, but only as long as the electrolyte near the cathode remains unsaturated with respect to the gas at 1 atm. pressure; under these conditions the hydrogen is being liberated at lower pressures and less negative potentials are adequate (cf. p. 310).

§ Tafel, *Z. physikal. Chem.*, 1900, 34, 200; 1905, 50, 641, 713; Lewis and Jackson, *ibid.*, 1906, 56, 193; Brunner, *ibid.*, p. 331; Bennett and

would have a potential of about -1.9 volts in a normal solution of hydrogen ions; * hence it is not necessary to postulate high pressures in order to account for overvoltages of the order of one volt. Knobel, Caplan and Eiseman † found that even at very high *C.D.*'s overvoltages do not exceed a value of about 1.3 volts, and so the partial pressure of atomic hydrogen at a cathode need only be a small fraction of one atmosphere.

The fact that overvoltage varies from one metal to another may be ascribed to their different catalytic influence on the reaction $2\text{H} \rightarrow \text{H}_2$, those with the lowest overvoltage, e.g. platinum and palladium, should be good catalysts, whereas lead and mercury should be poor catalysts. It is perhaps significant that by independent experiments made directly on atomic hydrogen, Bonhoeffer ‡ found the catalytic influence of various metals on the re-combination of the atoms to form hydrogen molecules decreased in the order platinum, palladium, tungsten, iron, chromium, silver, copper, lead and mercury: the parallelism of this order with that of increasing overvoltage is very striking. Since a catalyst must affect both direct and reverse reactions to the same extent, metals of low overvoltage should catalyse the reaction $\text{H}_2 \rightarrow 2\text{H}$; it is interesting to note in this connection that platinum, palladium and other low overvoltage metals are the best catalysts for hydrogenation purposes, in which the formation of atomic hydrogen is possibly an intermediate stage. Low overvoltage metals generally have a high adsorptive power for hydrogen § and consequently hydrogen atoms, resulting from the discharge of hydrogen ions, will attach themselves readily to the atoms of the metal; those atoms occupying adjacent positions are able to combine rapidly to form molecular hydrogen. High overvoltage metals, on the other hand, are poor adsorbents for hydrogen, and so the discharged atoms may occupy positions so far apart that their union in pairs becomes difficult; the atoms will thus accumulate and a high overvoltage results. It was first pointed out by Mott || that metals of low melting point have high overvoltages; in such metals the individual atoms in the solid must have a weak external field of force, since they can be readily separated from one another by heating. It may be concluded, therefore, that their adsorptive power for gases will be small. Metals of high melting point, on the other hand, should adsorb

Thompson, *J. Physical Chem.*, 1916, 20, 296; Bancroft, *ibid.*, p. 396; Allmand and Ellingham, *loc. cit.*; Glasstone, *Trans. Faraday Soc.*, 1924, 19, 808; Zlotowski, *Bull. Acad. Polonaise*, 1934 A, 143.

* See Bennett and Thompson, *loc. cit.*; Aten, *Trans. Amer. Electrochem. Soc.*, 1923, 43, 77.

† *Loc. cit.*

‡ *Z. physikal. Chem.*, 1924, 113, 199.

§ Cf. Caspari, *loc. cit.*; Thiel and Hammerschmidt, *loc. cit.*

|| *Trans. Amer. Electrochem. Soc.*, 1909, 15, 569.

gases to a considerable extent. All these facts are in harmony with the theory that the magnitude of the overvoltage is determined by the catalytic influence of the electrode material on the combination of hydrogen atoms.

It has been suggested from time to time that surface forces play some part in determining the actual overvoltage necessary for any particular metal, and there seems little doubt that the addition of certain substances which lower the liquid-gas interfacial tension have a definite effect both on the minimum overvoltage and that measured at an appreciable *C.D.* It is of interest, therefore, to see if such influences of surface forces might be correlated with the view under consideration concerning the cause of overvoltages. When the polarizing current applied to a cathode is gradually increased, provided the electrolyte is not saturated with hydrogen, it is observed that the potential increases rapidly at first but after a certain point the change of potential with increasing *C.D.* is relatively small (cf. Fig. 29): the point at which the inflexion occurs corresponds to that at which gas bubbles, containing gas at approximately atmospheric pressure, commence to be evolved. It is possible to argue, therefore, although this is not the only explanation of the facts, that the formation of bubbles of molecular hydrogen prevents the accumulation of atomic hydrogen. If the molecules of hydrogen as they are formed on the electrode by the combination of atoms remain attached to the metal surface then, to some extent, they will prevent pairs of atoms from approaching one another, and so the catalytic influence of the metal will be diminished: any factor, therefore, such as the formation of bubbles, which helps in the removal of hydrogen molecules will indirectly tend to diminish overvoltage.* It may be mentioned also that at high *C.D.*'s electrolytic hydrogen is in a chemically active condition,† and so the liberated bubbles probably contain some atomic hydrogen as well as the molecular form.

The pressure of gas which must be attained in the electrode surface before bubbles can be evolved probably depends on the tensions at three interfaces: electrode-gas, electrolyte-gas, and electrode-electrolyte; the first two oppose bubble formation, but the third aids the process. Any factors, therefore, decreasing the electrode-gas and electrolyte-gas tensions should decrease overvoltage, whereas a decrease of the tension at the electrode-electrolyte interface should increase the overvoltage; this is in general agreement with the observations already described (p. 427). It has also been shown by Möller ‡ that for a series of metals the minimum overvoltage varies in a manner parallel with the variation of angle

* See Glasstone, *Trans. Faraday Soc.*, 1925, **21**, 36, footnote.

† Grubb, *Nature*, 1923, **111**, 671.

‡ *Loc. cit.*

of contact between hydrogen bubbles and the metal in dilute sulphuric acid; this angle of contact is a function of the three interfacial tensions.* It is possible, therefore, that the overvoltage of hydrogen at a cathode is related to the surface forces and the ease of formation of gas bubbles. It is significant, also, that the overvoltage depends on the curvature of the cathode.† The reduction of surface forces at a roughened electrode may account partly for the observed decrease of overvoltage. The correlation of overvoltage with the ease of formation of bubbles is not necessarily in disagreement with the fact that only very minute amounts of electricity are required to establish relatively high overvoltages: it must be remembered that the observations were made with solutions, and electrodes, saturated with molecular hydrogen.

The theory that overvoltage is caused by the slowness of the combination of hydrogen atoms is in agreement with the independence of the minimum overvoltage of the hydrogen ion concentration of the electrolyte.‡ If c_H represents the concentration of atomic hydrogen at a polarized electrode when bubble formation commences, and $[H^+]$ is the hydrogen ion concentration of the electrolyte, then the electrode potential π_1 will be given by the equation (assuming activity coefficients equal to unity):

$$\pi_1 = \frac{RT}{F} \ln \frac{[H^+]}{kc_H} \quad (\text{iv})$$

The potential π_2 of a reversible hydrogen electrode, at a pressure of one atmosphere, in the same solution is expressed by

$$\pi_2 = \frac{RT}{F} \ln [H^+] \quad (\text{v})$$

The overvoltage ω is equal to $\pi_1 - \pi_2$, hence for any electrolyte

$$\omega = \frac{RT}{F} \ln \frac{1}{kc_H} \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{vi})$$

If the catalytic forces are not appreciably altered by changing the electrolyte then c_H will be a constant; hence the minimum overvoltage ω is also independent of the hydrogen ion concentration of the solution.

The relationship to be expected between overvoltage and *C.D.* was deduced by Tafel§ on the assumption that the rate of combination of hydrogen atoms was proportional to the square of their

* The angle of contact θ is given by the expression $\sigma_{1,2} \cos \theta = \sigma_{1,3} - \sigma_{2,3}$ where $\sigma_{1,2}$, $\sigma_{1,3}$ and $\sigma_{2,3}$ represent electrode-electrolyte, electrode-gas and electrolyte-gas interfacial tensions, respectively.

† Sederholm and Benedicks, *Z. Elektrochem.*, 1932, 38, 77.

‡ See, however, Herasymenko, *loc. cit.*

§ *Z. physikal. Chem.*, 1905, 50, 668; Westrip, *loc. cit.*

concentration, in accordance with the simple homogeneous reaction represented by $2\text{H} \rightarrow \text{H}_2$. If this is the case then when a stationary state is established at the electrode the current strength (I) is proportional to the rate of removal of hydrogen atoms to form molecules, assuming the amounts removed in other ways, e.g. diffusion or oxidation, are negligible; it follows, therefore, that

$$I = k_1 c_{\text{H}}^2 \quad \text{. (vii)}$$

and inserting this in equation (vi), there is obtained the relationship

$$\omega = a + \frac{RT}{2F} \ln I \quad \text{. (viii)}$$

where a is a constant. This is of the same form as equation (i), which is in agreement with experimental results, but the slope of the straight line obtained by plotting ω against $\log I$ should be $2.302RT/2F$, that is 0.029 at 18° , instead of the value of 0.12 , and even greater, frequently found in practice (p. 429). There are several ways in which this discrepancy may be accounted for: it may be necessary to distinguish between the hydrogen atoms on the electrode responsible for the potential and those actually adsorbed on the surface which determine the rate of combination. If the concentration of the latter is represented by $(c_{\text{H}})_s$, and if it is related to that of the former by the Freundlich isotherm, $(c_{\text{H}})_s = k_2 c_{\text{H}}^{1/n}$, then it can be readily shown that

$$\omega = a + \frac{nRT}{2F} \ln I \quad \text{. (ix)}$$

Since n is generally greater than unity the slope of the curve in which ω is plotted against $\log I$ would be greater than 0.029 at ordinary temperatures. Another possibility to be borne in mind is that the combination of hydrogen atoms may not be a second order reaction; since the process is a heterogeneous one, taking place on the electrode surface, it is possible for it to be apparently of the first, or even lower, order. The use of an order of less than two in equation (vii) would make the value of b in equation (i) greater than $2.3 \times RT/2F$; if the apparent order were 0.5 , then it would be $2.3 \times 2RT/F$, as found in a number of instances.

The influence of temperature on overvoltage is accounted for in the theory under consideration by its effect in increasing the velocity of the reaction $2\text{H} \rightarrow \text{H}_2$; its influence on surface forces may also be a contributory factor. The apparent constancy of the temperature coefficient of overvoltage, -0.002 volt/degree for many metals, led some authors* to suggest that the decrease in the magnitude of the surface forces is, in such cases, the main factor in the reduction of overvoltage with increasing temperature.

* See Harkins and Adams, *loc. cit.*

In addition to the formation of molecular hydrogen by the combination of two atoms there is another possible mechanism, namely by the interaction of a positive hydrogen ion either with a negative hydrogen ion, or something equivalent to it in the form of a hydrogen atom attached to the cathode surface and associated with an electron in some way.* According to Horiuti and Okamoto this mechanism must be regarded as an alternative to that considered above; both may occur simultaneously, and their relative extents depend on the conditions, e.g. electrode material and hydrogen ion concentration of electrolyte. From a consideration of the appropriate potential energy curves it can be shown that the alternative mechanism, involving reaction between a hydrogen ion, from solution, and a hydrogen atom and electron, on the metal, leads to a probable value of b in equation (i) equal to $2.3 \times 2RT/F$ as is frequently found. In view of the possibility that molecular hydrogen may be formed by both processes considered the value of b may vary from 0.029 to 0.12 at ordinary temperatures.

Bowden † has postulated that the dipoles consisting of positive and negative ions only escape from the surface as hydrogen molecules when they possess sufficient activation energy; this energy can be supplied either by increasing the temperature or by increasing the electrode potential. If w is the requisite activation energy of the dipoles when the electrode potential is zero, then when the latter is π , ‡ the energy may be taken to be $w - \alpha\pi F$, where πF is the electrical energy and α represents the fraction available for activation of the dipoles. When a steady state is attained the rate of activation, obtained from the Maxwell-Boltzmann distribution function, gives the rate of hydrogen evolution and hence it is proportional to the current; thus

$$I = ke^{-(w-\alpha\pi F)/RT} \quad . \quad . \quad . \quad . \quad . \quad (x)$$

Taking logarithms and re-arranging, this equation takes the form

$$\pi = a' + \frac{RT}{\alpha F} \ln I \quad . \quad . \quad . \quad . \quad . \quad (xi)$$

where a' is a constant: this gives the cathode potential, without the sign, in terms of the *C.D.*, and so subtracting the reversible hydrogen potential, a relationship similar to equation (i) is obtained for the overvoltage. Provided α has the reasonable value of 0.5,

* Heyrovský, *Rec. trav. chim.*, 1925, **44**, 499; 1927, **46**, 582; Bowden and Rideal, *loc. cit.*; Horiuti and Okamoto, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, 1936, **28**, 231. For a consideration of the mechanism of the reverse process, see Eley and Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 1388.

† *Proc. Roy. Soc.*, 1929, **126 A**, 107.

‡ The sign is not included in the potential, since the *numerical* value only of the energy is required.

the theoretical value of the slope b of the plot of ω against $\log I$ is equal to that observed. An examination of equations (x) and (xi) shows that a' , which may be used as a basis for comparing the overvoltages of different metals, is greater the greater is w , the energy of activation necessary for the formation of molecular hydrogen at zero potential. A low overvoltage metal is, therefore, one at which this energy is low, and hence it may be regarded as a catalyst for the process under consideration. By taking logarithms of equation (x) and differentiating with respect to temperature, at constant current, it is seen that

$$\frac{d\pi}{dT} = \frac{w - \pi T F}{\alpha F T} \quad \dots \quad (xii)$$

a simplified form of which has already been given (p. 431).

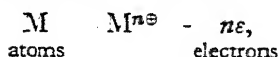
The suggestion that molecular hydrogen was formed by the interaction of positive and negative hydrogen ions was first made by Heyrovský to account for the variation of hydrogen overvoltage at the dropping mercury cathode with the pH of the solution: it was necessary to postulate that the potential of the electrode depended on the logarithm of the surface concentration of negative ions. The work of Bowden and Rideal has shown, however, that if these ions are present on the surface the potential must be *directly* proportional to their concentration, since the growth of potential in the early stages of hydrogen deposition is linear (p. 433). The same difficulty arises in connection with the simple theory that overvoltage is due to the accumulation of hydrogen atoms: if the electrode potential is related to the logarithm of the concentration of these atoms (equation iv), then the rate of increase of potential with the quantity of electricity passed, at the commencement of polarization, would be given by

$$d\pi/dQ \propto 1/c_H \quad \dots \quad (xiii)$$

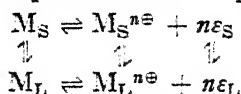
The rate of increase of potential should thus fall off as the hydrogen atoms accumulate, whereas actually $d\pi/dQ$ remains constant over a considerable range. It has been suggested, however,* that the electromotive behaviour of a substance in the form of a surface film may well be different from its behaviour in the bulk phase, and it is probable that in the former case the potential is proportional (numerically) to the surface concentration instead of to its logarithm. The rate of increase of potential with the quantity of electricity passed would thus be linear, as actually found. It may be pointed out that even if equation (iv) fails to give the electrode potential as far as the logarithm of the concentration of hydrogen atoms is concerned, it must still apply for the $\ln [H^+]$ term, so that the overvoltage should still be independent of the hydrogen ion concentration.

* Bowden and Rideal, *loc. cit.*

The alternative possibility that the slow discharge of hydrogen ions, that is the slow combination of the latter with electrons, is the cause of overvoltage was first considered in connection with the application by Smits of his theory of allotropy to the problem.* It was suggested that in every electrode there is an equilibrium between atoms, ions and electrons, thus :



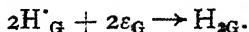
where n is the valency of the metal. If this electrode is placed in an electrolyte a heterogeneous equilibrium is instantaneously established between the ions and electrons in the metal and those in the solution; in addition there is probably a homogeneous equilibrium between atoms, ions and electrons in the electrolyte. The following scheme represents the complete equilibrium :



where the suffix S refers to concentrations in the electrode (solid) phase, and the suffix L to the electrolyte (liquid) phase; a similar equilibrium is supposed to exist between *gas* and electrolyte in the case of a hydrogen electrode. Smits† has shown that the difference of potential between an electrode and an electrolyte may be expressed by the general formula :

$$\pi = \frac{RT}{nF} \ln \frac{k_M [\text{M}_L^{n\oplus}]}{[\text{M}_S^{n\oplus}]}$$

where k_M is a constant for a given electrode material. If any metal is made a cathode then a stream of electrons is continually brought up to it; the positive ions with the lowest cathodic discharge potential, e.g. hydrogen ions, will be deposited instantaneously from the electrolyte on to the electrode. The following reaction will then tend to occur, either in the hydrogen gas phase or in the gas dissolved in the electrode :



If this reaction occurs slowly the hydrogen phase will be in a 'state of formation' and will contain an excess of ions and electrons over the equilibrium amounts. The value of $[\text{M}_S^{n\oplus}]$, in this case equal to $[\text{H}^{\cdot}_G]$, is greater than the equilibrium, or reversible, concentration and the electrode potential will become more negative than the reversible value; hence polarization, i.e. overvoltage, results. The metal of the electrode is considered to have some

* Smits, *The Theory of Allotropy*, Engl. trans., 1922, p. 115 *et seq.*; see also, *Z. physikal. Chem.*, 1935, 172, 470.

† *Op. cit.*, p. 119.

influence on the velocity of the combination of ions and electrons; a good catalyst for this process will presumably have a low hydrogen overvoltage.

The view that the slowness of the process of interaction between hydrogen ions and electrons is the cause of overvoltage has been proposed in a different form by Erdey-Grúz and Volmer,* in order to account for the fact that b in equation (i) is approximately equal to $2.3 \times 2RT/F$, that is about 0.116 at ordinary temperatures. If the ions brought up to the electrode by the current are not discharged immediately, but form with the electrons on the cathode a double layer which may be regarded as constituting two plates of a condenser, then the difference of potential across the double layer gives the measured electrode potential. During the course of the growth of this potential the hydrogen ions and electrons are brought up to the two plates of the condenser and so charge it. If during the building-up process practically no ions become discharged, the potential across the condenser will increase in direct proportion to the quantity of electricity passed, as actually found. The capacity of the condenser on the electrode surface should be independent of the material, in accordance with the suggestion of Bowden and Rideal. In order that the electron may pass across the double layer and so discharge a hydrogen ion, it is postulated that the doublet must acquire a certain activation energy; as the double-layer potential increases, the potential energy of the doublet is increased, and the requisite activation energy is correspondingly lowered. The rate of neutralization of hydrogen ions (Z_E) is given by the expression † (cf. equation x)

$$Z_E = k'c_+e^{-(U-\alpha nF)/RT} \quad \text{. (xiv)}$$

$$= kc_+e^{\alpha nF/RT} \quad \text{. (xiva)}$$

where c_+ is the surface concentration of hydrogen ions in the double layer, and U is the energy of activation necessary for ion discharge when there is no difference of potential between the metal and the solution. It is also necessary to consider the reverse of the above process, namely the transfer of electrons from neutral hydrogen atoms: if this is also influenced, in the opposite sense, by the double-layer potential, then the rate of formation of ions from atoms (Z_H) is given by

$$Z_H = k_1'c_H e^{-(W+\alpha nF)/RT} \quad \text{. (xv)}$$

$$= k_1c_H e^{-\alpha nF/RT} \quad \text{. (xva)}$$

where c_H is the concentration of hydrogen atoms and W is the requisite energy of activation for the ionization process at zero

* *Loc. cit.*

† As before, the sign is not included in the potential π : only the numerical value is used here.

potential. At a reversible hydrogen electrode, potential π_r , with no current flowing, Z_E and Z_H are equal, so that from equation (xiv) and (xv) it follows that

$$c_H = k_2 c_+ e^{2\pi_r F / RT} \quad (xvi)$$

where c_H represents the concentration of atomic hydrogen in normal equilibrium with molecular hydrogen at one atmosphere pressure. By means of equation (iv) it can be shown that the reversible hydrogen potential, excluding the sign, is related to this concentration by the expression *

$$c_H = k_3 [H'] e^{\pi_r F / RT} \quad (xvii)$$

where $[H']$ is the hydrogen ion concentration of the electrolyte. The quantity c_+ , the ion concentration on the electrode, will depend on $[H']$ and on the electrode potential, but if it is assumed as an approximation that it is independent of the latter, it follows on comparing equation (xvi) and (xvii) that α is equal to 0.5.† When a cathode is polarized the current flowing must be proportional to the difference between Z_E and Z_H , since this gives the net rate of formation of atoms, assuming there is no retardation of their union to form molecules, but for all except small overvoltages Z_H may be neglected in comparison with Z_E , and so

$$I = k_4 c_+ e^{\alpha \pi F / RT} \quad (xviii)$$

which is readily converted to the form

$$\omega = a + \frac{RT}{\alpha F} \ln I \quad (xix)$$

Since α is about 0.5, this is equivalent to equation (i) with b equal to $2.3 \times 2RT/F$, as required by experiment in several cases. The value of a depends on k_4 , and this on k (equation xiv), which in its turn includes U : the lower the overvoltage of the metal the smaller is the latter quantity. A low overvoltage metal is presumably, according to the theory, able in some way to reduce the energy which the ion-electron doublet must acquire before it can discharge itself to form an atom. Since c_+ is related to the hydrogen ion concentration of the solution, it is not difficult to show that the overvoltage will be independent of this concentration under the conditions for which equation (xviii) is applicable.‡ Since equation (xiv) is similar in form to equation (x), the variation of overvoltage

* Equation (iv) must apply to the equilibrium concentration of atomic hydrogen at the reversible potential, even if it is not applicable to the hydrogen atoms held on an electrode surface during electrolysis, as suggested above.

† For another derivation, see Frumkin, *Z. physikal. Chem.*, 1932, 160, 116.

‡ Cf. Essin, *ibid.*, 1933, 166, 270.

with temperature will be given by a relationship analogous to equation (xii).

Another theory, in a sense also involving the concept of slow neutralization of the charge on the hydrogen ion, in which the methods of quantum mechanics are used, has been developed by Gurney.* It is supposed that an energy barrier exists between the electrons in a metal and an ion approaching it, and according to classical mechanics the electron cannot cross the barrier to discharge the ion: quantum mechanics, however, allows of a definite probability of 'leakage' through the barrier of an electron from the cathode to an unoccupied level of the same energy in the ion to be discharged. If E_I is the ionization energy of the hydrogen atom, that is the energy required to yield an electron and a gaseous ion, and W is the energy of hydration of the latter, then the energy of ionization of the hydrated ion is $E_I - W$. Taking the energy of the separated atom and electron as zero, then the energy corresponding to the vacant electron level in the hydrated hydrogen is $E_I - W$ below the zero level. The work required to remove an electron from the cathode metal is related to its electronic (thermionic) work function, and may be represented by E_E so that the energy level occupied by an electron in the cathode may be taken as E_E below the zero energy level. If E_E is greater than $E_I - W$ it is evident that the highest occupied electron level in the cathode will be below the vacant level of the hydrated ion and neutralization of the latter cannot occur: in other words the ion cannot be discharged. By applying a potential π ,† however, the electron energy level in the metal is raised by an amount πF , and the necessary condition for the discharge of the ion is then

$$E_E + \pi F > E_I - W.$$

The actual state of affairs is more complicated than the simple picture given here, since firstly, not all the electrons in the metal are at one level, and secondly, the hydration energy can have a number of values corresponding to the different vibrational levels in the hydrated ion: that is to say, there are a number of electron energy levels in the cathode and a number of unoccupied levels in the ion. The distribution of the former is determined by the Fermi-Dirac statistics, whereas the latter is given by the Maxwell-Boltzmann law. In order to calculate the strength of the current which is able to pass at the given potential π , it is necessary to determine the rate of transfer of electrons through the barrier, and this is done by integrating the probability of transition of an

* *Proc. Roy. Soc.*, 1931, **134** A, 137; Fowler, *Trans. Faraday Soc.*, 1932, **28**, 368.

† As before, this does not include the sign.

electron from any level in the cathode to one of equal energy in the ion over the range of occupied levels. The result obtained by Gurney can be written in the form

$$\ln I = \frac{E_0 - E_E - \pi F}{\gamma RT} + \ln \frac{\gamma T}{\gamma - 1} + \text{const.} \quad (\text{xx})$$

where E_0 is the energy of neutralization of the hydrated ion in its lowest energy state, the energy of neutralization being defined by $E_1 - W - R$, where R is the repulsive energy between a hydrogen atom and a water molecule. The quantity γ is a factor which must be somewhat greater than unity: it allows for the fact that, owing to the operation of the Franck-Condon principle, the hydrogen atom and water molecule resulting from the discharge of the hydrated ion are not at rest, but have a certain amount of excess energy. This has the effect of reducing the range of overlapping energy levels, and allowance is made for it by introducing γ into the denominator. Equation (xx) is similar in form to the Tafel equation (i), and if γ is given the possible value of 2, the plot of π against $\log I$ should be equal to $2.3 \times 2RT/F$, in harmony with the experimental observations for certain metals. It appears, at first sight, from an examination of equation (xx) that the overvoltage should be connected with the electronic work function of the metal: this is, however, not the case. In order to obtain the overvoltage it is necessary to subtract the reversible hydrogen potential from π , and the former involves both E_0 and E_E , so that these terms cancel out. It is not clear from the quantum mechanical treatment what specific property of a metal affects its cathodic overvoltage. Observations on the rate of decay of hydrogen overvoltage and of the variation of the overvoltage at very low *C.D.*'s are in harmony with the wave-mechanical theory,* but they are probably explicable on the basis of other theories which postulate the presence of a double layer at the electrode surface.†

In reviewing the two main classes of theories of overvoltage it is seen that those based on the theory that the slow neutralization of the ion is the determining factor offer a more direct explanation of the fact that b in Tafel's equation is approximately $2.3 \times 2RT/F$: it must be remembered, however, that this value of b is by no means always applicable, although many authors have tacitly assumed it to be so (cf. p. 429). For a platinum cathode, especially when covered with platinum black, b is definitely less than the value given above,‡ but the view has been expressed that if perfectly

* Armstrong and Butler, *loc. cit.*; *J. Chem. Soc.*, 1934, 743; Butler, *Trans. Faraday Soc.*, 1933, 28, 379.

† See Volmer and Wick, *loc. cit.*

‡ Bowden and Rideal, *loc. cit.*; Baars, *loc. cit.*; Hammett, *J. Amer. Chem. Soc.*, 1924, 46, 7.

pure materials were used platinum would behave like other metals for which b is about 0.12 at ordinary temperatures. It is doubtful, however, if this is the case: Knorr and E. Schwartz * have found that for a palladium cathode the initial value of b is approximately 0.05, when the overvoltage is low; with continued use, however, the electrode becomes poisoned, the overvoltage rises, and b steadily approaches 0.12. Similar results have been obtained for platinum; with gradual poisoning b increases from 0.025 to 0.11.† It appears, therefore, that one mechanism is probably not sufficient to account for all the phenomena of overvoltage. Hammett ‡ has considered the consequence of supposing that discharge of the hydrogen ion and combination of resulting atoms may *both* be slow processes, and has deduced an equation, relating the current strength to the electrode potential, which at high overvoltages requires the slope of the potential against $\log I$ curve to be $2.3 \times 2RT/F$, whereas at low overvoltages it should be approximately $2.3RT/2F$. This means that when the overvoltage is low the determining factor is the rate of combination of hydrogen atoms to form molecules, but as the overvoltage increases the rate of discharge of the ions becomes of greater importance. The compromise between the two types of theory is very plausible, and may well prove more useful than either alone. The high values of b , such as have been found with lead in some electrolytes, however, still present a difficulty, and the rôle of surface forces may also require consideration.

Amongst various other theories § of overvoltage proposed from time to time, reference may be made to a modification of the atomic hydrogen theory. || The possibility is considered that the slow process may be the desorption of hydrogen atoms from the surface, and by simple thermodynamic treatment it is shown that the greater the work of desorption the smaller the overvoltage. A low overvoltage metal will have a large concentration of adsorbed hydrogen atoms as a result of the large amount of work required to remove these atoms from the surface. Such a metal will, therefore, be a good catalyst for chemical hydrogenation or reduction processes involving hydrogen gas, since these are heterogeneous and occur on the electrode surface. Low overvoltage cathodes are, however, known to have a low efficiency for electrolytic reduction (see p. 518): if it is assumed that in these processes the reduction takes place

* *Z. Elektrochem.*, 1934, 40, 38; *Z. physikal. Chem.*, 1936, 176, 161.

† Raeder and Nilsen, quoted by Knorr and Schwartz, *loc. cit.* (1936).

‡ *Trans. Faraday Soc.*, 1933, 29, 770.

§ Haber, *Z. Elektrochem.*, 1902, 8, 539; Newbery, *J. Chem. Soc.*, 1916, 109, 1359; Grube and Kleber, *Z. Elektrochem.*, 1924, 36, 517; Frölich and Clark, *ibid.*, 1925, 31, 649; Knibbs, *Trans. Faraday Soc.*, 1924, 19, 800; Sand, *ibid.*, 1930, 26, 19.

|| Kobosev and Nekrassov, *Z. Elektrochem.*, 1930, 36, 529.

in solution the effect can be explained, since the metal does not permit the escape of hydrogen atoms. The 'desorption potentials' of hydrogen atoms adsorbed on various metals have been measured* by determining the potential which must be applied to an electron stream impinging on the surface in order to render it capable of removing the adsorbed atoms; these potentials were found for the metals palladium, platinum, gold, tin and lead to be in the reverse order of their overvoltages. The desorption theory makes no attempt to account for the linear increase of potential during the process of charging the cathode, or for the value of b in Tafel's equation: it has nevertheless a number of interesting practical consequences.

Separation of Hydrogen Isotopes by Electrolysis—It was first pointed out by Washburn and Urey† that electrolysis of aqueous solutions results in the preferential liberation of the lighter isotope at the cathode, with the consequence that the residual electrolyte becomes richer in the heavy isotope, deuterium. This procedure is the one now widely adopted for the preparation of heavy water in comparatively large amounts.‡ If the relative rates of evolution of hydrogen and deuterium remain constant, irrespective of the composition of the water in the electrolyte, it is possible to write §

$$\frac{dN_H}{dN_D} = s \frac{N_H}{N_D} \quad \dots \dots \dots (xxi)$$

where N_H and N_D are the number of gm. mols. of hydrogen and deuterium in the electrolyte, and s is a constant known as the 'separation factor' or 'separation coefficient'. The quantity dN_H/dN_D represents the ratio of hydrogen to deuterium in the evolved gas, and N_H/N_D is the ratio for the liquid; consequently, the separation coefficient may be written in the form

$$s = \frac{[\text{Hydrogen}]_{\text{gas}}}{[\text{Deuterium}]_{\text{gas}}} \bigg/ \frac{[\text{Hydrogen}]_{\text{liquid}}}{[\text{Deuterium}]_{\text{liquid}}} \quad \dots \dots \dots (xxia)$$

which allows the value of s to be determined experimentally.

Although separation factors have been measured by a number of workers || it appears very difficult to obtain reliable data, since

* Kobosev and Anochin, *Z. physikal. Chem.*, 1931, B 13, 18.

† *Proc. Nat. Acad. Sci.*, 1932, 18, 496.

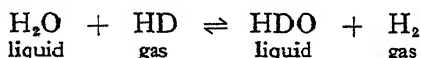
‡ For references, see *Ann. Reports Chem. Soc.*, 1934, 31, 13; 1935, 32, 40.

§ Lewis (G. N.) and Macdonald (J.), *J. Chem. Physics*, 1933, 1, 341.

|| Collie, *Nature*, 1933, 132, 568; Bell (R. P.), Wolfenden *et al.*, *ibid.*, 1934, 133, 25; *Proc. Roy. Soc.*, 1934, 144 A, 22; *J. Chem. Soc.*, 1936, 286; Topley and Eyring, *J. Chem. Physics*, 1934, 2, 217; Titani *et al.*, *Bull. Chem. Soc. Japan*, 1934, 9, 269; Eucken and Bratzler, *Z. physikal. Chem.*, 1935, 174, 279; Oddie, *Proc. Physical Soc.*, 1935, 47, 1060; Applebey and Ogden, *J. Chem. Soc.*, 1936, 163; Horiuti and Okamoto, *loc. cit.*

the results are often influenced by variations in factors not yet fully understood which occur during the course of electrolysis. A common value for s is about 6, this having been obtained both with low and high overvoltage cathodes in acid and alkaline electrolytes, but figures as low as 3, and as high as 17, or more, have been recorded. As a result of a comprehensive investigation, Eucken and Bratzler * have concluded that there is no obvious connection between the separation factor and the cathodic overvoltage, although certain catalytic poisons, e.g. alkaloids, increase the overvoltage, and at the same time lower the separation factor. Anodic pre-polarization of the cathode improves the separation efficiency; in one case a value as high as 19 was observed for the coefficient after this treatment. Increase of *C.D.* generally increases the separation factor, but this is not always the case. It may be recalled that equation (xxi) was based on the supposition that s is independent of the ratio of hydrogen to deuterium in the water, but it appears that, at least for a nickel cathode in an alkaline solution, it decreases as the deuterium content of the electrolyte is increased.†

Two circumstances tend to make the observed separation factors smaller than they should be: in the first place, the evolved gases are not dry, being saturated with both light and heavy water vapours, according to their pressures above the electrolyte. The separation factor for the vaporization of water is only 1.025, and so the apparent electrolytic separation factor observed with the wet gases will be lower than the true value for the dry gases. In the second place, the equilibrium



should theoretically be established whenever hydrogen and water are in contact, and consequently it should exist when hydrogen is evolved by electrolysis. The equilibrium constant

$$K = \frac{[\text{HDO}]_l [\text{H}_2]_g}{[\text{H}_2\text{O}]_l [\text{HD}]_g} = \frac{[\text{H}_2]_g}{[\text{HD}]_g} \bigg/ \frac{[\text{H}_2\text{O}]_l}{[\text{HDO}]_l} \quad (\text{xxii})$$

has a value of about 3.0 at ordinary temperatures, and a comparison of equations (xxia) and (xxii) shows that K is effectively the same as the separation factor, when it is remembered that for water containing less than 30 per cent. of the heavy form the deuterium in the liquid is mainly present as HDO and in the gas it is almost exclusively HD. If the equilibrium under consideration were established during electrolysis the separation factor should always be 3.0; for most electrodes it may be seen, from the observed values of s , that equilibrium is not attained, but at a platinized

* *Loc. cit.*

† Applebey and Ogden, *loc. cit.*

platinum cathode a separation factor of approximately 3 is generally obtained.* It is evident, however, that in any case there will always be a tendency towards the establishment of equilibrium, even if it is not actually reached: any separation factor above 3 will, therefore, tend to be decreased, the extent depending on the catalytic effect of the electrode material on the establishment of equilibrium. This is probably the main cause of the uncertain experimental results, which may consequently be of little theoretical significance as far as the fundamental problem of the separation of isotopes by electrolysis is concerned: the fact, however, that separation coefficients considerably larger than 3 are very common, means that there is a decided tendency for the preferential evolution of light hydrogen on electrolysis.

Calculations based on free energy changes show that this difference in behaviour between the two isotopes cannot be due to a difference in their reversible potentials, as this is quite small: it also cannot be due to the different mobilities of the hydrogen and deuterium ions, since the separation takes place equally well in alkaline and acid solutions although in the former the metal ions carry almost the whole of the current to the cathode. It must be concluded, therefore, that the electrolytic separation of hydrogen and deuterium is due to a difference in the retardation of the discharge of the ions to form molecules: that is to say, it is due to the different overvoltages for the two ions.† Few direct experiments have so far been made on the overvoltages necessary for the evolution of hydrogen and deuterium, but the limited observations, with a mercury cathode, show that it is definitely greater for the latter isotope.‡ It was thought at one time that observations on the separation factor for hydrogen and deuterium might throw light on the theory of overvoltage and distinguish between the two possible causes, namely slowness of ionic discharge, or slowness of combination of the atoms, but this has proved not to be the case. It was first suggested§ that the second of these processes was responsible for the separation of the hydrogen isotopes, but R. P. Bell|| has argued that since the value of s is almost independent of the electrode material, slowness of the neutralization of the ions is more likely to be the underlying cause. This conclusion is in harmony with Gurney's quantum mechanical theory of overvoltage, since the relative rates of evolution of hydrogen and

* Washburn, Smith (E. R.) and Frandsen, *Bur. Stand. J. Res.*, 1933, 11, 453.

† For discussion, see Fowler, *Proc. Roy. Soc.*, 1934, 144 A, 452.

‡ Bowden and Kenyon, *Nature*, 1935, 135, 105; Heyrovský and Müller (O. H.), *Coll. Czech. Chem. Comm.*, 1935, 7, 281.

§ Sherman and Eyring, *J. Chem. Physics*, 1933, 1, 345.

|| *Ibid.*, 1934, 2, 164.

deuterium will depend only on the difference in the neutralization energies of the two ions, and this, which is equal to the difference in the zero-point energies of the ions, is independent of the electrode material. The separation factor calculated from the approximately known difference in zero-point energies is approximately 4, which is much less than has been often observed. Other calculations have been made on the basis of the assumption that the difference in the rates of evolution of hydrogen and deuterium on electrolysis is determined either by the slowness of the neutralization of the ions,* or by the delay in the combination of the atoms: † in every case separation factors of the order of 10 ± 5 , in agreement with those obtained experimentally, have been evaluated theoretically, and it is therefore evident that the results do not permit of a clear choice between the two main theories of overvoltage. It may be noted that an observed separation factor of about 100 has been reported from a solution containing only a small proportion of deuterium: ‡ if this is confirmed it may have important consequences,§ although it probably has no bearing on the theory of overvoltage.

* Topley and Eyring, *loc. cit.*; Urey and Teal, *Rev. Mod. Physics*, 1935, 7, 34.

† Urey and Teal, *loc. cit.*; Halpern and Gross (P.), *J. Chem. Physics*, 1935, 3, 452; Okamoto, Horiuti and Hirota, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, 1936, 29, 223.

‡ Applebey and Ogden, *loc. cit.*

§ Horiuti and Polanyi, *Acta Physicochimica U.R.S.S.*, 1935, 2, 522; see also, Bawn and Ogden, *Trans. Faraday Soc.*, 1934, 30, 432.

CHAPTER XVIII

THE DEPOSITION OF METALS

CATHODIC Deposition of Metals—It has been seen (p. 417) that as a general rule metals commence to be deposited at their reversible potentials, and at very small *C.D.*'s the discharge of positive ions may be regarded as a reversible process. At increasing *C.D.*'s the cathode potential becomes slightly more negative,* partly as a result of concentration polarization and partly on account of the slowness of one or other of the stages which must be involved between the initial discharge of the ion and the final orientation of the atom in the space lattice of the metal crystal. Volmer † has put forward the view that when the metal ion reaches the cathode it is not discharged immediately, but remains on the surface in a form intermediate between that of the hydrated ion in the solution and that of the atom in its final state in the crystal. As a result of lateral movement over the surface the ion reaches a suitable point in the lattice where it is instantaneously discharged. ‡ From a study of the current-potential curves obtained during the deposition of a number of metals, the conclusion has been reached that the actual neutralization of the ion occurs rapidly, and that the observed polarization is determined by the rate of formation of crystallization nuclei by spreading across the electrode surface. § If the cathode is of the same material as the metal being deposited, the points at which the ions on the surface are able to participate in the free electrons are reached without great difficulty, and polarization is not considerable. When the electrode is different from the metal being deposited, however, the deposition potential may be initially in excess of that required when it is covered with deposit, since there is no crystal lattice in which the ions can be

* Le Blanc, *Abh. Bunsen-Ges.*, 1910, No. 3.

† *Z. physikal. Chem.*, 1928, 139, 597; Brandes, *ibid.*, 1929, 142, 97; see, however, Hunt (L. B.), *Trans. Amer. Electrochem. Soc.*, 1934, 65, 95.

‡ According to Dr. R. W. Gurney (private communication) metal deposition differs from gas deposition in showing little or no overvoltage (with few exceptions) because immediately the ions take their place in the space lattice of the metal they are able to participate in the free electrons.

§ Erdey-Grúz and Volmer, *Z. physikal. Chem.*, 1931, 157, 165; see also, Erdey-Grúz, *ibid.*, 1935, 172, 157.

discharged immediately.* The anions present in the solution influence to some extent the polarization associated with metal deposition, and it is possible that they may prevent access of the ions to the points in the lattice at which they can be discharged.†

The deposition of metals from solutions of complex cyanides undoubtedly commences at the reversible potential, but in some cases, e.g. copper and zinc, marked polarization is observed which was at one time attributed to the slowness of the dissociation of the complex into simple ions. It is now suggested, however, that this is mainly due to concentration polarization; the marked increase in cathode potential is attributed to the fact that in some circumstances a small change in the ratio of metal to free cyanide in solution causes a large alteration of potential.‡ With copper and zinc further complications arise since the cathode potential soon reaches the point at which hydrogen evolution can commence; the current efficiency for metal deposition then decreases rapidly and the cathode exhibits almost the same potential as if hydrogen only were being liberated.

Polarization of quite a different type occurs in the deposition of iron, cobalt and nickel from solutions of their simple salts; even at extremely small *C.D.*'s deposition does not commence until the cathode potential is distinctly more negative than the reversible value.§ The approximate deposition and reversible potentials from *N*-solutions of sulphates of the three metals are given in Table LXIV.

TABLE LXIV

DEPOSITION AND REVERSIBLE POTENTIALS IN *N*-SULPHATE SOLUTIONS

Metal.	Reversible Potential.	Deposition Potential.		
		15°	55°	95°
Iron .	- 0.46	- 0.68	- 0.49	- 0.46
Cobalt .	- 0.28	- 0.56	- 0.46	- 0.36
Nickel .	- 0.23	- 0.57	- 0.43	- 0.29

Nickel deposition from a chloride solution has been observed at a cathode potential of - 0.40 volt at 18°,|| but it is doubtful

* Erdey-Grúz and Volmer, *ibid.*, 1931, 157, 182; Erdey-Grúz and Wick, *ibid.*, 1932, 163, 63; Samarcev and Evstropiev, *Bull. Acad. Sci. U.R.S.S.*, 1934, 603.

† Cf. Müller (E.) and Barchmann, *Z. Elektrochem.*, 1933, 39, 341.

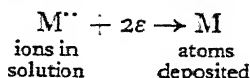
‡ Glasstone, *J. Chem. Soc.*, 1929, 690, 702; 1930, 1237; see also Essin and Matanzev, *Z. physikal. Chem.*, 1935, 174, 384.

§ Schweitzer, *Z. Elektrochem.*, 1909, 15, 602; Schildbach, *ibid.*, 1910, 16, 967; Foerster, *Abh. Bunsen-Ges.*, 1909, No. 2; Glasstone, *J. Chem. Soc.*, 1926, 2887.

|| See Foerster and Georgi, *Z. physikal. Chem., Bodenstein Festband*, 1931, 453.

whether it takes place much closer to the reversible potential, even at very low *C.D.*'s. The polarization effect decreases with increasing temperature, and in fact above 70° iron deposits reversibly, except for factors such as those mentioned above connected with the growth of metal layers.

To account for the irreversibility in the deposition of the iron-group metals, Foerster* suggested that the ionic discharge process



occurs slowly, and is further retarded by the hydrogen liberated simultaneously with the deposition of metal (*vide infra*). Smits,† however, considered that since this process is a heterogeneous one it should be instantaneous: this author considered that the retardation of metal deposition is due to the slowness with which ions and electrons come into equilibrium in the electrode itself, in the presence of various negative catalysts, particularly hydrogen. A different rôle is attributed to the hydrogen by Kohlschütter,‡ who suggested that a film of the gas on the electrode prevents the growth of the small crystals of metal; thus the latter is deposited in a highly dispersed form with a high free energy, and an excess potential is required to cause the ions to discharge. This form of metal would be in a state of strain and so there will be a tendency for it to change into a stable form; this may account for the known strains in nickel deposits and for the tendency of the layers to peel off from the electrode. Frölich and Clark§ have shown that metals which deposit reversibly, e.g. mercury and lead, have a high hydrogen overvoltage, whereas iron, nickel and cobalt have a low overvoltage. If the overvoltage may be ascribed to the formation of hydrides, as was at one time suggested,|| then it may be supposed that the hydrides of the latter group are stable and that deposition of metal does not occur until its hydride has accumulated to a sufficient extent to decompose rapidly, and hence polarization results.

According to all the views outlined the initial deposition potential of the iron-group metals might be expected to vary with the hydrogen ion concentration of the electrolyte, or the hydrogen gas concentration at the electrode. The deposition potential, however,

* *Z. Elektrochem.*, 1916, 22, 85.

† See *Theory of Allotropy*, 1922, pp. 132, 334; *Trans. Faraday Soc.*, 1924, 19, 772.

‡ See *Trans. Amer. Electrochem. Soc.*, 1924, 45, 229, for summary and references.

§ *Z. Elektrochem.*, 1925, 31, 649.

|| See, for example, Newbery, *J. Chem. Soc.*, 1916, 109, 1359.

appears to be independent of the hydrogen ion concentration of the solution and of the gas concentration. It has been suggested* that iron, cobalt and nickel are initially deposited from solution in an active metastable state with a different electronic arrangement from that of the ordinary metals. The actual deposit would consist of a solid solution of both stable and metastable forms, and should be deposited at a more negative potential than the reversible value for the stable metal. On increasing the temperature the rate of transformation of metastable to stable form is increased; the solid solution then contains a larger proportion of the latter, and the deposition potential approaches the reversible value. According to this view hydrogen gas and hydrogen ions play no direct part in the cathodic process of metal deposition, although simultaneous evolution of hydrogen probably has some influence on the state of strain observed in the deposits. The theory suggested by Le Blanc† also attributes no part to hydrogen; it is considered that dehydration of the ions in solution must occur before they can be discharged. If the dehydration process occurs slowly, polarization will result, and a higher cathodic potential will be required in order to cause deposition of the metal. The main objection to this view is that it would require not so much a large irreversibility for the initial deposition occurring at a very slow rate, but rather a rapidly growing polarization with increasing *C.D.*, and increasing rate of metal deposition. In actual practice, however, it is found that once electrodeposition has commenced, the cathode potential does not vary much more with increasing *C.D.* than does that of a copper electrode in copper sulphate solution.‡ This objection applies to all theories dependent on the slowness of a *chemical* reaction velocity, but does not affect the concept of the transformation of the metal from a metastable to stable form.

If no particular part is attributable to hydrogen gas or hydrogen ions the observations might be explained by assuming that the combination of the metal ion with an electron occurred slowly, as suggested in somewhat different ways by Foerster and by Smits. This view has been considered by Thon,§ who postulated the necessity of a certain energy of activation for the discharge process, similar to that required for the neutralization of hydrogen ions (p. 442): this activation is apparently not necessary for metals such as zinc, cadmium, copper, silver, etc., which commence to deposit at their reversible potentials. There still remains to be

* Glasstone, *loc. cit.*

† *Trans. Faraday Soc.*, 1914, 9, 251; see also Newbery, *J. Chem. Soc.*, 1917, 111, 470; *Proc. Roy. Soc.*, 1928, 119 A, 680; *J. Amer. Chem. Soc.*, 1929, 51, 1429; Isgarishev and Berkmann, *Z. Elektrochem.*, 1922, 28, 40.

‡ Glasstone, *loc. cit.*

§ *Compt. rend.*, 1933, 197, 1312.

explained, however, why the ions of iron, cobalt and nickel are not able to participate in the free electrons of the cathode whereas other metals are able to do so.

Depolarization of Metal Deposition—If the metal which is being deposited can form a solution in the cathode or, better, form a compound with it which dissolves in the cathode material, then the solution pressure (or free energy) of the deposited metal is reduced; hence deposition can occur at a potential which is *less* negative than the reversible value. The most striking example of this type of depolarization is the deposition of sodium, or potassium, on a mercury cathode, from a neutral or alkaline solution. The reversible deposition potential of sodium from a normal solution of its ions is about -2.7 volts, but sodium will commence to be deposited on a mercury cathode at much less negative potentials. The sodium probably combines with mercury to form one or more compounds, and these subsequently dissolve in the mercury cathode; since the electrode potential of sodium amalgam is markedly less negative than that of pure sodium,* appreciable deposition occurs at a potential of -1.2 volts. In a neutral solution of a sodium salt the reversible potential for hydrogen ion discharge is -0.4 volt, but at a mercury cathode there is an overvoltage of about 0.8 volt; hence the evolution of hydrogen gas does not *commence* until the cathode potential attains -1.2 volts. It is clear, therefore, that owing to the high overvoltage at a mercury cathode, and the marked depolarization of the latter on the discharge of sodium ions, a simultaneous deposition of sodium and hydrogen is possible; thus dilute amalgams may be prepared by the electrolysis of aqueous alkali chloride solutions. These principles have been applied in technical processes for the manufacture of sodium hydroxide from brine by electrolysis; the alkali amalgam is subsequently decomposed by water.†

Depolarization by a solid cathode may also occur, but as the alloy formed is unable to diffuse rapidly into the bulk of the electrode—as is the case with mercury—the surface soon becomes saturated; the depolarization effect is not then so marked as with mercury. In spite of this it is not improbable that sodium ions can be discharged at a lead electrode from alkaline solutions; sodium-lead alloys of low cathodic potential appear to be formed, and the subsequent decomposition of these alloys may be responsible

* Haber and Sack, *Z. Elektrochem.*, 1902, 8, 251; Haber, *ibid.*, p. 541; Sack, *Z. anorg. Chem.*, 1903, 34, 286; Kremann *et al.*, *Z. Metallkunde*, 1920, 12, 414, 444; Stender *et al.*, *Trans. Amer. Electrochem. Soc.*, 1935, 61, 23.

† For details, consult Allmand and Ellingham, *Applied Electrochemistry*, 1924, p. 397; Engelhardt, *Handbuch der technischen Elektrochemie*.

for the disintegration of the lead cathode with the formation of dark clouds of finely divided metal.*

Simultaneous Deposition of Two Metals †—When a solution contains two or more kinds of positive ions, then on electrolysis the deposit may contain one or both of the metals (or hydrogen) depending on circumstances. This subject is of importance since all aqueous solutions contain a positive ion—hydrogen ion—in addition to any metallic ion which may be present. The reversible potential of an electrode producing positive ions in a solution containing these ions at activity a is given by

$$\pi = \pi_0 - \frac{RT}{nF} \ln a.$$

If ω is the overvoltage ‡ or irreversibility of deposition—this includes all types of polarization—at any given *C.D.*, then the deposition of metal at that *C.D.* occurs at a potential given by

$$\pi = \pi_0 - \omega + \frac{RT}{nF} \ln a.$$

For a solution containing two kinds of positive ions, represented by suffixes A and B, the deposition potentials will be

$$\pi_A = \pi_{0A} - \omega_A + \frac{RT}{n_A F} \ln a_A \text{ and } \pi_B = \pi_{0B} - \omega_B + \frac{RT}{n_B F} \ln a_B$$

respectively. On passing current through such a solution, ion discharge will occur as soon as the cathode potential just exceeds the deposition potential of the more positive metal. The actual nature of the deposit will depend on the relation between the various factors involved, viz. standard electrode potentials, overvoltages and ionic activities (or concentrations). The general behaviour of solutions can be described in two main groups, when the deposition potentials are (a) far apart, or (b) close together. The assumption is made that the two metals A and B do not form a compound or solid solution with one another, or with the cathode material.

Case I.— π_A is much less negative than π_B —The *C.D.*—cathode potential curves are shown in Fig. 32; at all reasonable *C.D.*'s the deposit will consist of pure A, since the potential required for deposition of B is not attained. This is the condition

* Bredig and Haber, *Ber.*, 1898, 31, 2741; Haber and Sack, *loc. cit.*

† For theoretical study, see Essin, *Z. physikal. Chem.*, 1933, 164, 87.

‡ The term overvoltage as used here applies not only to gases, but to irreversibilities such as are observed in the deposition of the iron group metals; it is equal to the difference between the observed deposition potential and the reversible value in the same solution.

necessary for the quantitative separation of metals by electro-deposition (p. 460); it is only realized if one metal is appreciably more noble than the others, or if the activities of the others are reduced by the formation of complex ions. Thus, the electrolysis of a neutral solution of copper sulphate yields copper at 100 per cent. efficiency; if excess of cyanide is added to the solution, however, hydrogen is discharged preferentially. In many cases the rate of deposition of the more noble element is so high that it exceeds the rate at which it can be brought up to the electrode by diffusion. In order to maintain the flow of current other ions must be discharged, and the cathode potential then becomes rapidly more negative until the discharge potential of the other ions is reached. For this reason a copper-zinc alloy can be deposited at high *C.D.*'s from a mixed solution of copper and zinc sulphates;

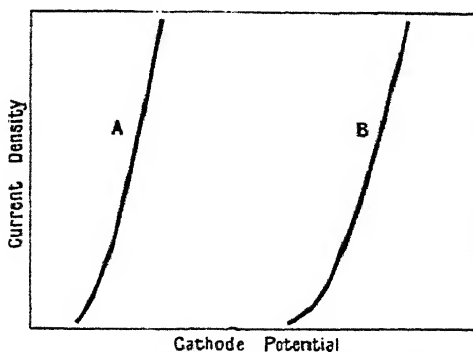


FIG. 32.—Cathode potentials for two metals when alloy deposition does not occur

at low *C.D.*'s, however, copper exclusively is deposited.* Similar observations have been made with copper and cadmium, silver and cadmium, silver and zinc, copper and lead, and copper and iron; in some instances compound formation may aid the deposition of the baser metal.†

Case II.— π_A and π_B are approximately equal—In these circumstances both substances may be deposited simultaneously; this will occur (a) if the standard potentials are close together and polarization small; (b) if the difference in overvoltage brings the deposition potentials closer together than are the reversible potentials; and (c) if the concentration of the ions of the more noble metal is reduced. Examples of these three cases are well known. (a) The normal potentials of lead and tin are -0.12 and -0.134

* Cf. Sauerwald, *Z. anorg. Chem.*, 1920, 111, 243.

† Tammann, *ibid.*, 1919, 107, 226; Creutzfeldt, *ibid.*, 1921, 121, 25.

volt respectively ; since these metals are discharged almost reversibly, only a small adjustment of ionic concentration is sufficient to allow simultaneous deposition to occur from chloride or fluoborate solutions.* If the solution is acid, then theoretically hydrogen should be liberated, since its normal potential is ± 0.0 volt ; but on account of the high hydrogen overvoltage at lead and tin cathodes nearly the whole of the current will be used in the deposition of the metals. (b) The deposition potential of zinc is about -0.77 volt from a *N*-solution ; hence from a neutral or acid solution hydrogen discharge should occur more readily than zinc deposition ; the hydrogen overvoltage at a zinc cathode is, however, of the order of -0.7 to -0.8 volt, and so the deposition potentials are brought together. Zinc and hydrogen may therefore be deposited simultaneously on a zinc cathode. If an aluminium cathode is used, since the hydrogen overvoltage is lower, a much higher *C.D.* must be applied before zinc commences to be deposited ; with a platinum electrode a still higher *C.D.* is required. In these cases hydrogen discharge at first occurs preferentially, but once enough zinc has been deposited to cover the electrode there is a rapid increase of hydrogen overvoltage and zinc deposition occurs more readily.† The simultaneous deposition of hydrogen with nickel and cobalt from almost neutral solutions is due to the overvoltage of the deposition of these metals ; if it were not for this they would be deposited alone. For iron the circumstances are somewhat different, as the reversible deposition potential of iron from a neutral solution (about -0.44) is approximately equal to that for hydrogen in the same solution (-0.40) ; simultaneous deposition could only be avoided if the overvoltages were markedly different, but this is not the case. (c) Although the normal deposition potentials of zinc and copper, and of cadmium and copper are far apart, they may be brought together by adjustment of the ionic concentrations. If potassium cyanide is added to solutions of salts of these metals, complex cyanides are formed ; the cuprocyanide ion is the most stable of these complexes and the cuprous ion concentration is reduced to such an extent that its reversible potential approaches those of zinc and cadmium in cyanide solutions. The deposition potentials quoted in Table LXV will make the matter clear ; they show that copper and zinc, and copper and cadmium may deposit simultaneously from complex cyanide solutions even at low *C.D.*'s.‡

* * Lehmann, *Z. physikal. Chem.*, 1889, 4, 325 ; Blum (W.) and Haring, *Trans. Amer. Electrochem. Soc.*, 1921, 40, 147.

† Tainton, *ibid.*, 1922, 41, 389.

‡ For other examples, see Masaki, *Bull. Chem. Soc. Japan*, 1932, 7, 158.

TABLE LXV

DEPOSITION POTENTIALS FROM SULPHATE AND COMPLEX CYANIDE SOLUTIONS

	Sulphate.	Complex Cyanide + Free Cyanide.
Copper	+ 0.34	- 1.0
Cadmium	- 0.40	- 0.9
Zinc .	- 0.76	- 1.1

In any of the three types of cases considered the *C.D.*-cathode potential curves lie close together, but they may be related to one another in three different ways: (i) the separate curves for metals A and B are more or less parallel (Fig. 33, I); (ii) the curves diverge at increasing *C.D.* (Fig. 33, II); (iii) the curves converge, cross

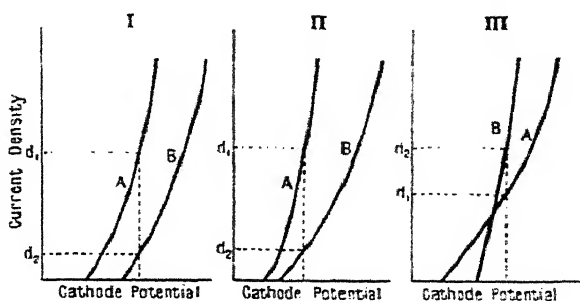


FIG. 33.—Cathode potentials for two metals when alloy deposition is possible

and then diverge (Fig. 33, III). If the metal A is the more noble it alone may be deposited until the *C.D.* is reached at which the potential corresponds to the deposition of B; both metals are then deposited simultaneously. A further increase of *C.D.* results in both metals being deposited in proportions which depend on the form of the curves; in general, however, the metal A deposits at a rate proportional to d_1 and B to d_2 , where d_1 and d_2 are the *C.D.*'s at which A and B, respectively, have the same cathode potentials.

Under any given conditions, therefore, the fraction $\frac{d_1}{d_1 + d_2}$ of the total current will be utilized in depositing A, and $\frac{d_2}{d_1 + d_2}$ in the

deposition of B, and the deposit will contain A to B in the ratio of d_1 to d_2 equivalents. In Fig. 33 (I) $d_1 - d_2$ is almost constant, and d_1/d_2 decreases with increasing *C.D.*; the proportion of A then decreases as the *C.D.* is raised; in Fig. 33 (II) d_1/d_2 remains almost constant and so also will the composition of the deposit. If, as in Fig. 33 (III), the curves cross, then d_1 and d_2 are equal at this

point and the deposit consists of equivalent amounts of A and B; below this *C.D.* the deposit contains excess of A, and above it excess of B. It must be emphasized that these deductions assume that there is no impoverishment of either ion in the vicinity of the cathode; in actual practice such impoverishment always occurs, and operates in favour of the deposition of the less noble metal.

Simultaneous Deposition of Compounds or Solid Solutions—Hitherto it has been assumed that the two elements being deposited simultaneously do not form compounds or solid solutions; the actual behaviour is not always so simple. The formation of an entirely new phase on the electrode, with its own deposition potential, may vitiate any conclusions drawn from a study of the individual components. The reversible potential of a solid solution generally lies in between those of the pure constituents (p. 496); hence an alloy containing both elements may be deposited at a potential much less negative than that deemed necessary for the less noble constituent. This is undoubtedly the explanation of the fact that on electrolysis of a mixed solution of nickel and magnesium sulphates the deposit invariably contains about 2 per cent. of magnesium, although its deposition potential is about -1.7 volt.* The deposition of zinc-nickel alloys at potentials of about -0.6 volt is less striking, but is probably due to the same cause. In general, the initial deposit obtained at very low *C.D.*'s would be expected to contain an excess of the more noble constituent, whereas at high *C.D.*'s, as the negative potential of the electrode increases, the deposit should contain increasing amounts of the less noble metal; in any case the composition of the deposit also depends on the ratio of the ionic concentrations of the two metals in the electrolyte.† Many other factors may, however, have to be taken into consideration where polarization phenomena occur.‡

Quantitative Separation of Metals by Electrolysis §—Although the idea that metals could be separated quantitatively by means of an electric current was used as far back as 1864,|| and the importance of adjusting the applied *E.M.F.* was realized by Kiliani in 1883,** it was not till Le Blanc had published the results

* Coehn, *Z. Elektrochem.*, 1902, 8, 593; Siemens, *Z. anorg. Chem.*, 1904, 41, 249.

† For examples, see Creutzfeldt, *loc. cit.*

‡ E.g. Glasstone *et al.*, *Trans. Faraday Soc.*, 1927, 23, 213; 1928, 24, 370; 1930, 26, 565; 1931, 27, 29; 1932, 28, 733; 1933, 29, 426.

§ For full details consult: Classen, *Quantitative Analyse durch Elektrolyse*; Fischer (A.), *Elektroanalytische Schnellmethoden*; Smith (E. F.), *Electroanalysis*; Treadwell, *Elektroanalytische Methoden*; Böttger, *Physikalische Methoden der analytischen Chemie*, Vol. II.

|| Wolcott Gibbs, *Z. analyt. Chem.*, 1864, 3, 334; see also Luckow, *Dingl. polyt. J.*, 1865, 177, 296.

** *Berg- und Hüttenmännische Ztg.*, 1883.

of his work on deposition potentials (p. 416) that the theoretical basis of the separation could be made clear.* It is now known that, apart from polarization effects, a metal commences to be deposited from a given solution when the cathode potential is made slightly more negative than the reversible potential in that solution; thus if one litre contains 1 gm. mol. of each of simple salts of silver, copper and cadmium the deposition of the metals will commence at $+0.79$, $+0.32$ and -0.40 volt, respectively. Hence by regulating the applied *E.M.F.*, and thus the cathode potential, the silver may be deposited almost completely before copper deposition commences; similarly copper may be entirely separated from cadmium. These separations are, of course, contingent upon the metals not forming compounds or solid solutions under the conditions of deposition. Since the concentration of the ions of deposited metal decreases during electrolysis, its deposition potential becomes steadily more negative, and may eventually approach that for the deposition of another metal; thus if the ionic concentration is reduced to 0.1 per cent. of its original value, the potential becomes 3×0.029 volt more negative for a bivalent metal and 3×0.058 volt for a univalent metal. The initial deposition potentials of two metals should thus differ by at least 0.2 volt for a quantitative separation, within the limits of analytical error, to be practicable.†

Experimental Method—The method devised by Freudenberg for separating two metals was to apply an *E.M.F.* to two electrodes placed in a given solution, so that the cathode potential was just more positive than that at which the second metal begins to deposit. A considerable improvement was made by Sand,‡ who introduced an auxiliary standard electrode, e.g. $\text{Hg}|\text{Hg}_2\text{SO}_4(s)\text{H}_2\text{SO}_4$, or calomel electrode, so that the potential of the cathode could be accurately controlled;§ the potentiometer-voltmeter method (p. 389) was used for direct measurement of potential. A current (3–10 amps.) is passed through the solution and the cathode potential measured at the commencement of electrolysis; as the ions are removed by deposition the current requires adjustment (decrease) in order that the cathode potential should be kept constant. When the current has fallen to a low value (about 0.2 amp.), the applied

* Freudenberg, *Z. physikal. Chem.*, 1893, 12, 97.

† It will be realized that, in any case, a complete separation of two metals is theoretically never possible.

‡ *J. Chem. Soc.*, 1907, 91, 373; 1908, 93, 1572; *Trans. Faraday Soc.*, 1909, 5, 159. For later developments, see Lassieur, *Bull. Soc. Chim.*, 1926, 39, 1167; Sand, *Analyst*, 1929, 54, 275; Lindsey and Sand, *ibid.*, 1934, 59, 328; 1935, 60, 739.

§ For convenient forms of electrode vessel, see Smith (T. B.), *Trans. Faraday Soc.*, 1928, 24, 216; Sand, *loc. cit.*

E.M.F. is increased so that the cathode potential becomes 0.1 to 0.2 volt more negative. In this way the concentration of the metal is reduced to less than 0.1 per cent. of its original value; there is no danger of a second metal being deposited provided its deposition potential is not within 0.2 volt of that of the first. In a modification of the Sand method of control, Brown* used as an auxiliary electrode a wire of the metal being deposited; the potential of the cathode was always kept within -0.1 to -0.2 volt of that of the auxiliary electrode.

To expedite the process of metal deposition—in the so-called ‘rapid electroanalysis’—the solution is stirred; † by this means a higher *C.D.* may be used, and the rate of deposition of ions still kept below that at which they diffuse to the cathode from the bulk of the electrolyte. If the rate of diffusion cannot keep pace with the deposition, discharge of other ions will occur and the results may be vitiated. Increase of temperature favours diffusion and so moderately high temperatures are frequently used. Electrodes of wire gauze were introduced by Paweck‡ and are now in general use since they allow rapid mixing to occur. It should be noted that as the ions are removed from solution during electrolysis the rate of diffusion, which may be regarded as proportional to the concentration in the bulk of electrolyte, must fall; a gradual decrease of *C.D.*, such as occurs in the method of Sand, is therefore desirable.

In many cases where the ordinary deposition potentials of two metals differ by 0.2 volt, or less, and a satisfactory separation is not possible in the ordinary way, special methods of adjusting the potentials may be used; two examples are of interest. Copper and bismuth cannot be separated electrolytically from solutions of their simple salts; if cyanide is added, however, the copper ions form a complex cuprocyanide and the deposition potential is much more negative than before. The bismuth ion concentration and electrode potential are hardly affected, and a separation from copper becomes possible.§ If an ammoniacal solution containing zinc and nickel is electrolysed at 18° an alloy is obtained, but at 90°

* *J. Amer. Chem. Soc.*, 1926, 48, 582.

† Gooch and Medway, *Amer. J. Sci.*, 1903, 15, 320; Exner, *J. Amer. Chem. Soc.*, 1903, 25, 896; Fischer (A.), *Z. angew. Chem.*, 1907, 20, 138; Sand, *loc. cit.*; Frary, *Z. Elektrochem.*, 1907, 13, 308; Fischer, Thiele and Stecker, *ibid.*, 1911, 17, 905; Edgar and Purdum, *J. Amer. Chem. Soc.*, 1922, 44, 1267; see also general references at the head of this section (p. 460).

‡ *Chem.-Ztg.*, 1898, 24, 855; Winkler, *Ber.*, 1899, 32, 2192.

§ Smith (E. F.), *Amer. Chem. J.*, 1890, 12, 428; Sand, *loc. cit.* (1907); compare the separation of cadmium and cobalt from complex cyanide solution: Freudenberg, *loc. cit.*; Classen, *op. cit.*, p. 321.

complete separation of the nickel by electrodeposition is possible.* The overvoltage for nickel deposition is considerably reduced as the temperature is raised; hence at 90° it separates at a much more positive potential than does zinc. At ordinary temperatures the deposition potentials are very close, and a separation cannot be realized.† The difficulty of separation in this case, as in many other instances, is probably accentuated by the tendency of the metals to form solid solutions.

The cathode material is usually of platinum gauze, but amalgamated brass, copper and other metals have been used; ‡ E. F. Smith and his co-workers have found that in certain cases mercury has distinct advantages as a cathode material.§ For anode platinum gauze is also used; the presence of chlorides in the solution should be avoided as the liberated chlorine may attack the platinum which is then deposited on the cathode.

Before concluding the subject of electrolytic separation of metals, mention must be made of lead, manganese and cobalt, which under suitable conditions separate on the *anode* as PbO_2 , MnO_2 and Co_2O_3 respectively.**

Physical Nature of Electrodeposited Metals ††—The form in which a metal is deposited on the cathode depends on the conditions of deposition; for example, silver is obtained as large crystals from nitrate solutions, but as a fine-grained smooth deposit from complex cyanide solutions. It is generally agreed that electrodeposited metals are crystalline; the external appearance depends mainly on the rate at which the crystals grow and on the rate of formation of fresh nuclei. If the conditions are such as to favour

* Hollard and Bertiaux, *Bull. Soc. Chim.*, 1904, 31, 102.

† Foerster, *Z. Elektrochem.*, 1907, 13, 563.

‡ See, for example, Paweck and Walther, *Z. anal. Chem.*, 1924, 64, 89.

§ See *J. Amer. Chem. Soc.*, 1903, 25, 883; Lukens, *Trans. Amer. Electrochem. Soc.*, 1927, 52, 309; Tutundžić, *Z. anorg. Chem.*, 1931, 202, 297; 1933, 215, 19; Böttger *et al.*, *Z. anal. Chem.*, 1933, 93, 401.

|| See, however, Schoch and Brown, *J. Amer. Chem. Soc.*, 1916, 38, 1660.

** Lead: Exner, *loc. cit.*; Fischer and Boddaert, *Z. Elektrochem.*, 1904, 10, 945; Sand, *Trans. Faraday Soc.*, 1909, 5, 207; Manganese: Engels, *Z. Elektrochem.*, 1895, 2, 413; 1896, 3, 286; Gooch and Kobayshi, *Amer. J. Sci.*, 1917, 44, 53; Cobalt: Coehn and Glaser, *Z. anorg. Chem.*, 1903, 33, 9.

†† For deposition of metals from non-aqueous solutions, see Röhler, *Z. Elektrochem.*, 1910, 16, 419; Müller (R.), *Monatsh.*, 1924, 44, 219; 1925, 45, 525; Taft and Barham, *J. Physical Chem.*, 1930, 34, 929; Audrieth and Yntema, *ibid.*, p. 1903; Booth and Merlub-Sobel, *ibid.*, 1931, 35, 3303; Chaney and Mann, *ibid.*, p. 2289; Stilwell and Audrieth, *J. Amer. Chem. Soc.*, 1932, 54, 472; for reviews, see Müller (R.), *Ahren's Sammlung*, 1924, 27, 243; Audrieth and Nelson, *Chem. Reviews*, 1931, 8, 335.

the rapid formation of crystal nuclei the deposit will be fine-grained, whereas a tendency for rapid growth of crystals will produce a rough deposit containing visible crystals; these large crystals usually grow along the 'current lines', i.e. towards the anode, probably because this results in a decrease of resistance. The chief factors influencing the deposit are (i) *C.D.* of electrodeposition; (ii) concentration of electrolyte; (iii) temperature; (iv) nature of the electrolyte; (v) nature of basis metal; and (vi) presence of colloidal matter. These factors will be considered in turn.*

Current Density—At very low *C.D.*'s the discharge of ions occurs slowly, and so the rate of crystal growth should exceed the rate of formation of nuclei; under these conditions the deposit should be, and generally is, coarsely crystalline. At higher *C.D.*'s the rate of nucleus formation increases† and the deposit will become more fine-grained. At very high *C.D.*'s, however, the solution in the vicinity of the cathode becomes depleted of ions required for discharge; these must diffuse up from the bulk of the solution, and the resulting local differences of concentration cause irregularities in the growth of the deposit. This production of 'trees', nodules, or protruding crystals is favoured by the consequent decrease in the distance through which an ion has to diffuse, and by the decrease of resistance between anode and cathode at these points. In many cases the *C.D.* is increased to a stage at which the rate of deposition exceeds the maximum rate of diffusion of ions in the given solution; discharge of another ion, e.g. hydrogen, must occur to maintain the current and gas evolution may commence. Bubble formation frequently interferes with crystal growth, and porous and spongy deposits result. Further, hydrogen ion discharge causes the cathode solution to become alkaline with consequent precipitation of hydroxides and basic salts; these may be included in the deposit and will affect crystal growth so that very fine and dark, or 'burnt', deposits result.‡

Concentration of Electrolyte—The effect of electrolyte con-

* Bancroft, *Trans. Amer. Electrochem. Soc.*, 1904, 6, 27; 1912, 21, 329; 1913, 23, 266; Blum (W.), *ibid.*, 1919, 36, 213; Blum and Rawdon, *ibid.*, 1923, 44, 397; Graham, *ibid.*, 1927, 52, 157; Hunt (L. B.), *J. Physical Chem.*, 1931, 35, 1006; Foerster, *Elektrochemie wässriger Lösungen*, 1922, p. 384 *et seq.*; Allmand and Ellingham, *Applied Electrochemistry*, 1924, p. 120 *et seq.*; Blum and Hogaboom, *Electroplating and Electroforming*, 1930, Chap. VII; Hughes (W. E.), *Electrodeposition of Metals*, 1923.

† See, Glazunov, *Z. physikal. Chem.*, 1934, 167, 399; cf. also Kohlschütter *et al.*, *Z. Elektrochem.*, 1924, 30, 72; 1927, 33, 277, 290; 1932, 38, 213.

‡ Faust, *Z. anorg. Chem.*, 1912, 78, 201; Sieverts and Wippelmann, *ibid.*, 1915, 91, 1; 93, 287; Kohlschütter and Toropoff, *Z. Elektrochem.*, 1913, 19, 161; Arndt, *Ber.*, 1929, 62, 80; O'Sullivan, *Trans. Faraday Soc.*, 1930, 26, 89; see also references already given.

centration and of *C.D.* may be regarded as complementary ; if the concentration is large the roughening of the deposit may be delayed until a very high *C.D.* is reached, since impoverishment of the cathode solution does not occur readily. In a concentrated solution, too, the presence of many ions may increase the tendency for nucleus formation,* and firm, adherent deposits are obtained.† It may be noted that as a result of an important study Glazunov ‡ has concluded that increase of concentration decreases the rate of formation of crystal nuclei ; it also decreases their rate of growth in a direction perpendicular to the cathode but increases the rate at which they grow over the surface. With a very dilute electrolyte the rate of discharge of ions may exceed the rate of diffusion to the cathode at quite low *C.D.*'s ; hence burnt, rough or spongy deposits are generally obtained. If the solution is stirred, however, the rate of diffusion of ions is increased and better deposits result.§ Stirring has the effect of raising the *C.D.* at which hydrogen begins to be evolved, and not only improves the deposit but also raises the current efficiency for metal deposition ; for these reasons agitation is frequently employed in commercial electroplating practice.

Temperature—Increase of temperature has two effects which oppose one another ; in the first place it favours diffusion and so tends to produce a uniform, fine deposit, but on the other hand it increases the rate of crystal growth and aids the formation of coarse deposits. At moderate temperatures the influence of the first factor generally predominates, but at higher temperatures the second is increasingly operative. Since increase of temperature decreases hydrogen overvoltage, evolution of gas may occur at a lower *C.D.* ; where such evolution is liable to occur, e.g. in the deposition of zinc, the deposit tends to become spongy.

Nature of Electrolyte—Several aspects of this factor must be considered, although some of them are at present inexplicable. If the electrolyte is a poor conductor, there will be a tendency for 'trees' and other growths to form in the direction of the anode. The addition of a good conductor, e.g. sodium chloride, will generally eliminate this effect. The nature of the anion present appears to have an important influence ; thus from lead nitrate solution rough deposits are obtained, but smooth ones result in perchlorate, silico-

* There is no agreement on this point, see Foerster, *op. cit.*, p. 389, and Blum and Rawdon, *loc. cit.*

† Glaser, *Z. Elektrochem.*, 1901, 7, 365, 381 ; Pfannhauser, *ibid.*, 1902, 8, 41.

‡ *Loc. cit.*

§ Zimmermann, *Trans. Amer. Electrochem. Soc.*, 1903, 3, 245 ; Bennett, *ibid.*, 1912, 21, 253.

fluoride and borofluoride solutions.* Similar observations have been made in the deposition of silver and other metals.† The valency state of the metal may affect the form of the deposit; from plumbic solutions lead is deposited in a spongy form, but from plumbous solutions comparatively large crystals are produced.‡ In a similar manner smooth, uniform deposits of tin are obtained from stannate, but from stannite solutions they are unsatisfactory.§

An outstanding fact in connection with metal deposition is that solutions of complex ions, e.g. cyanides and tartrates, generally yield smooth, fine-grained deposits; the reason for this is by no means clear. Some authors|| consider that nucleus formation is favoured by the extremely small concentration of simple ions present in the solution of complex ion, although 'treeing' is prevented by the good conductance. Kohlschütter** has suggested that some of the insoluble salt, e.g. cyanide, is deposited with the metal and hence prevents crystal growth. Others have attributed the uniformity of the deposit from complex cyanide solutions to the discharge of ions other than the simple metal ions; radicals so formed either decompose or react with the solution and deposit the metal.†† The best deposits of chromium are undoubtedly obtained from a solution of chromic acid containing a small amount of sulphate ions: the nature of the deposit is apparently influenced by the presence of a complex chromic chromate diaphragm on the cathode surface.‡‡

Nature of Basis Metal—Until recently the influence of the basis metal on the structure of the electrodeposit was not fully realized; several observations have now been made which indicate that in general the orientation of the crystals, at least in the first layers of the deposit, is a continuation of that in the basis

* Senn, *Z. Elektrochem.*, 1905, 11, 229; Fischer, Thiele and Maxted, *Z. anorg. Chem.*, 1910, 67, 302, 339; Mathers, *Trans. Amer. Electrochem. Soc.*, 1910, 17, 261; *ibid.*, 1919, 36, 235. For discussion, see Hunt (L. B.) *loc. cit.*; *J. Physical Chem.*, 1932, 36, 2259.

† Eisenreich, *Z. physikal. Chem.*, 1911, 76, 691; Brunck, *Z. angew. Chem.*, 1911, 24, 193; Müller (E.) and Barchmann, *Z. Elektrochem.*, 1933, 39, 341; Schlötter, *Trans. Faraday Soc.*, 1935, 31, 1177.

‡ Elbs and Rixon, *Z. Elektrochem.*, 1903, 9, 267.

§ Foerster, *op. cit.*, p. 392; Oplinger, *Metal Ind.* (New York), 1931, 29, 529; Hothersall, Clarke (S. G.) and Macnaughtan, *J. Electroplat. Dep. Soc.*, 1934, 9, 101.

|| See Blum and Rawdon, *loc. cit.*; Blum and Hogaboom, *op. cit.*

** *Z. Elektrochem.*, 1913, 19, 181; see also, Macnaughtan and Hothersall, *Trans. Faraday Soc.*, 1935, 31, 1168; Glasstone, *ibid.*, p. 1218.

†† Cf. Glasstone, *J. Chem. Soc.*, 1929, 690; see also, *idem.*, *loc. cit.* (1935).

‡‡ For recent discussions of this complicated subject, see Pfanhauser and Elssner, *Z. Elektrochem.*, 1931, 37, 874; Müller (E.), *ibid.*, 1934, 40, 73; Liebreich, *ibid.*, p. 874.

metal.* The external form of the deposit is rarely affected by the basis metal.

Influence of Colloidal and other Addition Agents †—The presence of very small amounts of colloidal matter, or of certain organic compounds, often has a profound effect on the nature of the electrodeposit; in general the metal so obtained is smooth, fine-grained and micro-crystalline,‡ whereas in the absence of colloidal matter large crystals may be obtained.§ Only a small amount, of the order of 0.05 gm. per litre, of addition agent is necessary in order to produce an improvement in the deposit; if an excess is added the crystals are so small that the deposit may become loose and powdery, or brittle. Amongst the materials used are gelatine, peptone, agar, rubber, dextrin, gum tragacanth, gum arabic, casein, glucosides, alkaloids, dyestuffs, clove oil, glue, extract of aloes, lactic acid, camphor, sugars, glycine and aluminium salts; the action of any particular agent is specific and depends on the nature of the metal and of the electrolyte. The good deposits obtained from silicofluoride solutions have been attributed to colloidal silica resulting from hydrolysis; and the presence of small amounts of various metallic hydroxides results similarly in improved silver and nickel deposits.**

* Blum (W.) and Rawdon, *Trans. Amer. Electrochem. Soc.*, 1923, **44**, 305; Graham, *ibid.*, pp. 310, 427; *ibid.*, 1927, **52**, 157; Frölich and Clark (G. L.), *ibid.*, 1926, **49**, 369; *Z. Elektrochem.*, 1925, **31**, 649; Frölich, Clark and Aborn, *ibid.*, 1926, **32**, 295; Tammann and Straumanis, *Z. anorg. Chem.*, 1928, **175**, 131; Foerster and Klemm, *Z. Elektrochem.*, 1929, **35**, 409; Wood (W. A.), *Proc. Physical Soc.*, 1931, **43**, 138; Portevin and Cymboliste, *Trans. Faraday Soc.*, 1935, **31**, 1211; Hothersall, *ibid.*, p. 1242.

† For review, see Sand, *Brit. Assoc. Fourth Rep. Colloid Chem.*, 1922, p. 345.

‡ Foerster, *Z. Elektrochem.*, 1897, **4**, 163; 1898, **5**, 512; Müller (E.) and Bahntje, *ibid.*, 1906, **12**, 317; Senn, *loc. cit.*; Marc, *Z. physikal. Chem.*, 1909, **67**, 410; **68**, 104; 1910, **73**, 685; 1911, **75**, 710; 1912, **79**, 71; 1913, **81**, 641; *Z. Elektrochem.*, 1913, **19**, 431; Freundlich and Fischer (J.), *ibid.*, 1912, **18**, 885; Kohlschütter and Schacht, *ibid.*, 1913, **19**, 172; Pring and Tainton, *J. Chem. Soc.*, 1914, **105**, 710; Mathers *et al.*, *Trans. Amer. Electrochem. Soc.*, 1912, **21**, 313; 1913, **24**, 315; 1914, **25**, 319; 1914, **26**, 99; 1915, **27**, 131; 1916, **29**, 417; 1917, **31**, 271; Kern and Capillon, *ibid.*, 1924, **45**, 409; Fuseya *et al.*, *ibid.*, 1926, **50**, 235; 1927, **52**, 249; Frölich *et al.*, *loc. cit.*; Arndt, *loc. cit.*; Milliau, *Bull. Soc. Chim. Belg.*, 1925, **34**, 143; Clark (B.) and Jones (E. O.), *Trans. Faraday Soc.*, 1929, **25**, 583; Taft *et al.*, *J. Physical Chem.*, 1931, **35**, 2585; 1932, **36**, 2338, 2446.

§ e.g. Lead: Marc, *loc. cit.*; Tin: Foerster and Deckert, *Z. Elektrochem.*, 1930, **36**, 901; Silver: Wernick, *Trans. Faraday Soc.*, 1928, **24**, 361; Cadmium: *idem.*, *ibid.*, 1935, **31**, 1237.

|| See, for example, Marc, *loc. cit.*, 1913; Sieverts and Wippelmann, *loc. cit.*

** Kohlschütter and Schacht, *loc. cit.*; O'Sullivan, *loc. cit.*; Macnaughtan and Hothersall, *loc. cit.*

In some manner, not clearly understood, the addition agent prevents the growth of crystals on the cathode; the agent may be adsorbed by the crystal nuclei, or deposited on them by cataphoresis, or deposited as a complex with the metal ion. The result is that the rate of crystal growth is reduced or the free access of ions to the cathode, necessary for crystal growth, is restricted by the presence of a film of coagulated colloid. It is significant that the deposits generally contain a certain proportion of the addition agent; the mechanism of its action is not, however, understood.* Some parallelism has been found between the decrease of crystal size resulting from the addition of a given substance to an electrolytic bath and the 'protective effect' of that substance in preventing coagulation of a colloidal solution of the metal; † the latter process involves the *aggregation* of crystals, and the former *growth* of crystals. ‡

Polarization and Nature of Deposit—Various attempts have been made to correlate the nature of the electrodeposit with the extent of cathodic polarization occurring during deposition of the metal; § it is often considered that the greater the polarization the finer the crystals in the deposit, but it is rather doubtful whether the connection is so simple. Many factors influence the cathodic potential which apparently have no influence on the deposit, whereas other factors affect the deposit but make no appreciable change in polarization; consequently it often seems quite impossible to correlate polarization with the type of deposit obtained.||

Other Physical Properties—Physical properties of electrodeposits other than of external form, e.g. hardness and strain, frequently vary with the condition of deposition; this subject has been studied mainly in connection with silver and with the metals iron, cobalt and nickel, but no satisfactory generalizations have yet appeared.**

* Bancroft, *Trans. Amer. Electrochem. Soc.*, 1912, 21, 239; Blum, *loc. cit.*; Kohlschütter and Schacht, *loc. cit.*; Grube and Reuss, *Z. Elektrochem.*, 1921, 27, 45; Frölich, *loc. cit.*, 1924; Fuseya, *loc. cit.*, 1926; Marie and Jacquet, *Compt. rend.*, 1928, 187, 41; Kersten, *J. Physical Chem.*, 1931, 35, 3644; Jacquet, *Compt. rend.*, 1935, 201, 953.

† Müller and Bahntje, *loc. cit.*; Wernick, *loc. cit.*

‡ See Discussion, *Trans. Faraday Soc.*, 1929, 25, 13.

§ Cf. Aten and Boerlage, *Rec. trav. chim.*, 1920, 39, 720; Blum and Rawdon, *loc. cit.*; Haring, *Trans. Amer. Electrochem. Soc.*, 1926, 49, 417; Kohlschütter, *ibid.*, 1924, 45, 229; Clark and Jones, *loc. cit.*; Foerster and Deckert, *loc. cit.*

|| Graham, *loc. cit.*; Macnaughtan and Hothersall, *Trans. Faraday Soc.*, 1928, 24, 497; Glasstone and Sanigar, *ibid.*, 1929, 25, 590; 1931, 27, 309; Glasstone, *ibid.*, 1935, 31, 1232.

** Vuilleumier, *Trans. Amer. Electrochem. Soc.*, 1922, 42, 99; Kohlschütter, *loc. cit.* (summarizing paper); Sanigar, *Trans. Faraday Soc.*, 1929, 25, 1; Macnaughtan and Hothersall, *loc. cit.* (1928); Glasstone and Sanigar, *loc. cit.*

Throwing Power *—This factor is of importance in technical electroplating; it may be described as the property of a solution by virtue of which a relatively uniform deposit of metal may be obtained on a cathode of irregular surface. From a theoretical standpoint it seems that throwing power should be influenced mainly by (a) the rate of increase of cathode potential with *C.D.*, and (b) the conductance of the solution.† Should preferential deposition occur at any part of the cathode then the effective *C.D.* in this vicinity will be higher than on the rest of the electrode; if this higher *C.D.* requires a much increased cathode potential in order to maintain it, whereas the *E.M.F.* applied to the cell remains constant, there will be a tendency for the *C.D.* to be reduced at the part under consideration. It seems, therefore, that a cathode potential-*C.D.* curve with a marked slope should favour a uniform current distribution, and so should correspond with good 'throwing power'. The observations of Haring and Blum ‡ appear to favour this view; increase of temperature and stirring tend in many cases to reduce polarization at high *C.D.*'s and hence cause a decrease in throwing power.§ The addition of colloids increases polarization and also throwing power. It may be mentioned that although there is very little change in cathode potential with *C.D.* during the deposition of silver from argentocyanide solutions containing excess of cyanide,|| the throwing power appears to be good; the subject requires further study.

The conductance of the electrolyte is important; if the resistance is high the current lines will tend to concentrate on the parts of the cathode nearest to the anode and throwing power will be bad. With a solution of low resistance, however, there will be no appreciable tendency for deposition to occur at any particular portion of the electrode. As a general rule the conductance of an electrodeposition bath is sufficiently good to have no definite effect on throwing power.

The Mercury Dropping Cathode—A special technique involving a cathode which is being continuously renewed has been devised by Heyrovský for the study of electrolytic phenomena; **

* For chief study and references see Haring and Blum (W.), *Trans. Amer. Electrochem. Soc.*, 1923, **44**, 313; also Heatley, *ibid.*, p. 283; Haring, *ibid.*, 1924, **46**, 107; Arndt and Clemens, *Chem.-Ztg.*, 1922, **46**, 925; Kaneko, *J. Soc. Chem. Ind. Japan*, 1931, **34**, Suppl. bind., No. 4, 135; Bussi, *Z. Elektrochem.*, 1932, **38**, 783, Mantzell, *ibid.*, 1935, **41**, 10; 1936, **42**, 303.

† In certain cases the efficiency of metal deposition has a direct or indirect influence on 'throwing power', see Haring, *loc. cit.*

‡ *Loc. cit.*

§ See, however, Arndt and Clemens, *loc. cit.*

|| Glasstone, *J. Chem. Soc.*, 1929, 690; Glasstone and Sanigar, *loc. cit.* (1929).

** *Phil. Mag.*, 1923, **45**, 303.

the apparatus used is represented diagrammatically in Fig. 34. Through a stopper in the flask *A* (capacity 50–100 c.c.) is inserted a thick-walled capillary tube *B*; the latter terminates below the level of the liquid in *A*, and mercury from a reservoir *C*, falling from the end of this tube at the rate of 20 to 30 drops per minute acts as cathode. The mercury layer *D* at the bottom of the flask is the anode, connection being made by means of a sealed-in platinum wire. The solution is always saturated with hydrogen before an experiment—since reducible substances cause errors—by passing in the gas at the side-tube *E* and out through a trap. The anode and cathode are connected to the positive and negative poles of a polariz-

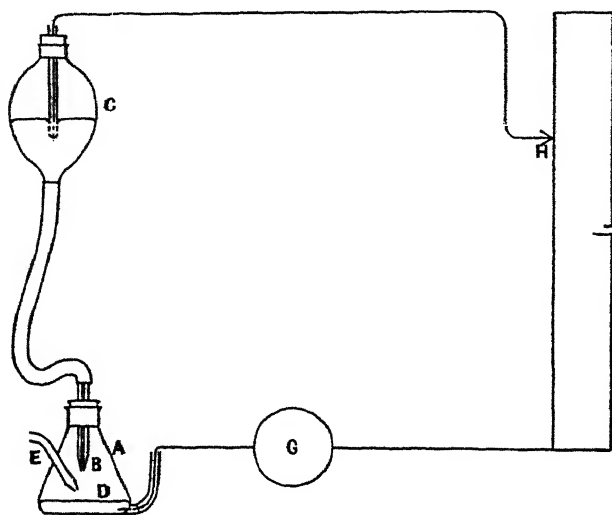


FIG. 34.—The dropping mercury electrode

ing battery *F*, and the applied voltage varied by moving the contact *H*; the current flowing is indicated by a d'Arsonval galvanometer (*G*) and the value of the *E.M.F.* across *BD* is determined. Since the anode has a large area and the current is generally very small, of the order of 10^{-6} amp., the polarization at this electrode is negligible and its potential may be regarded as constant; if this is measured by comparison with a standard calomel electrode, the cathode potential can be determined from the total *E.M.F.* across the cell. The values of cathode potential for various polarizing currents can be plotted in the usual manner, and a sudden rise of current, without an appreciable increase of potential, indicates the discharge of an ion; each separate ion produces a 'wave' in the current-potential curve, and the height of the wave, in terms of

current, is proportional to the concentration of the ion.* An automatic apparatus called a 'polarograph' has been developed † by means of which the polarizing *E.M.F.* is steadily varied; the value of the current flowing is registered on a synchronized rotating drum. This apparatus has been used in all subsequent work by Heyrovský and his collaborators. The mercury dropping cathode method of studying deposition potentials, and polarization curves in general, is claimed to have the following advantages; (a) as the mercury has a high overvoltage hydrogen evolution does not occur readily, and many metals, even sodium and potassium, may be deposited; (b) the continual dropping of the mercury means a regular renewal of the cathode surface and concentration polarization is eliminated; (c) the drops falling on the anode cause stirring to occur there; and (d) the bottom layer keeps a well-defined potential and can be used as a reference electrode.

Deposition Potentials by the Drop Electrode—The deposition potentials obtained by this method are generally lower, i.e. less negative, than the reversible values, as deposition is depolarized by dissolution in, or compound formation with, the mercury; in some cases the deposition potentials appear to be more negative than the reversible values. The changes resulting from dilution, viz. 0.058 and 0.029 volt for a ten-fold change with uni- and bivalent ions respectively, are in agreement with theoretical requirements. The main exception to this rule has been found in the discharge of hydrogen ions, ‡ and is attributed to the variation of overvoltage with the hydrogen ion concentration of the electrolyte; various other measurements (see pp. 427, 432), however, lead to the conclusion that overvoltage is generally independent of the hydrogen ion concentration, and it has been suggested that the mechanism of the dropping electrode is too complicated for it to be comparable with a stationary electrode.§ It has been claimed that the *separate* deposition from mixed solutions of iron and nickel, and of nickel and cobalt, can be observed with the dropping mercury cathode,|| whereas in ordinary electrolysis the metals deposit simultaneously as an alloy; ** this constitutes an important difference

* Heyrovský, *Trans. Faraday Soc.*, 1924, 19, 692.

† Heyrovský and Shikata, *Rec. trav. chim.*, 1925, 46, 496.

‡ Herasymenko, *ibid.*, p. 503; *Z. Elektrochem.*, 1928, 34, 129; Herasymenko and Šlendyk, *Z. physikal. Chem.*, 1930, 149, 123; 1932, 162, 223.

§ See Lloyd, *Trans. Faraday Soc.*, 1930, 26, 12; Bowden, *ibid.*, 1928, 24, 473; Herasymenko, *ibid.*, 1931, 27, 203; Andauer and Lange (E.), *Z. physikal. Chem.*, 1933, 162, 241; Frumkin, *ibid.*, 1933, 164, 121; Glidden and Patrick, *J. Amer. Chem. Soc.*, 1933, 55, 3594.

|| Emelianova, *Rec. trav. chim.*, 1925, 46, 528.

** Cf. Glasstone, *J. Chem. Soc.*, 1926, 2897; Glasstone and Symes, *Trans. Faraday Soc.*, 1927, 23, 213.

between dropping and stationary electrodes which requires explanation.

Apart from the investigations of deposition potentials and polarization curves the dropping mercury cathode has been used for analysing solutions as dilute as 10^{-6} molar,* for the study of hydrogen ion concentrations, for determining valency changes during deposition or electrolytic reduction,† and for determining the stability constants of complex ions.‡ Abnormal maxima are frequently observed in the polarization curves and have been attributed to the presence of reducible substances or of materials absorbed by the mercury;§ the existence of these maxima, together with the differences between the dropping and stationary cathodes already mentioned, suggest that results obtained with the dropping electrode are not necessarily universally applicable.||

* See Heyrovský, *Bull. Soc. Chim.*, 1927, 41, 1224; *Mikrochem.*, 1932, 12, 25; Prát, *Biochem. Z.*, 1926, 175, 268; Majer, *Z. anal. Chem.*, 1933, 92, 321, 401; *Z. Elektrochem.*, 1936, 42, 120, 123.

† Herasymenko, *Z. Elektrochem.*, 1928, 34, 74, 129.

‡ Pines, *Coll. Czech. Chem. comm.*, 1929, 1, 387.

§ Sanigar, *Rec. trav. chim.*, 1925, 46, 549; Emelianova and Heyrovský, *Trans. Faraday Soc.*, 1928, 24, 257; Herasymenko, *ibid.*, pp. 267, 272; Heyrovský and Šimůnek, *Phil. Mag.*, 1929, 7, 951; see, however, Ilkovič, *Coll. Czech. Chem. Comm.*, 1932, 4, 460.

|| For other researches with the mercury dropping cathode see *Trans. Faraday Soc.*, 1924, 19, 721; 1925, 21, 42, 53; 1928, 24, 272; 1929, 25, 152; *Compt. rend.*, 1924, 179, 1044, 1267; 1926, 183, 125; *Rec. trav. chim.*, 1925, 46, 488-607; *J. Chem. Soc.*, 1928, 301; *J. Chim. physique*, 1929, 26, 219; *Bull. Soc. Chim.*, 1929, 45, 30; series of papers in *Coll. Czech. Chem. Comm.*, 1929 et seq. by Heyrovský and collaborators; in *Mem. Coll. Agric. Kyoto*, 1927 et seq. by Shikata et al.; and in *Gazzetta*, 1932 et seq. by Semerano and co-workers. For reviews, see Kernula, *Z. Elektrochem.*, 1931, 37, 779; Böttger, *Physikalische Methoden der analytischen Chemie*, Vol. II, p. 260 (Heyrovský); Semerano, *Il Polarografo*, 1932.

CHAPTER XIX

IRREVERSIBLE ANODE PHENOMENA

IF the process : $\text{metal} \rightleftharpoons \text{ions} + \text{electrons}$ is reversible, an anode of that metal should begin to dissolve when the applied potential is just greater than the reversible value in the given solution. A copper anode in a molar solution of copper sulphate commences to enter solution when its potential is just more than $+0.32$ volt ; if the *C.D.* is increased there will be a certain amount of concen-

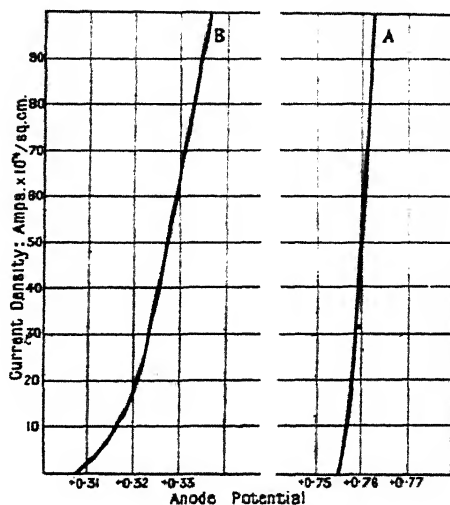


FIG. 35.—Anode potentials of mercury (A) and copper (B)

tration polarization, and consequently a more positive anode potential will be required for metal dissolution to continue. The increase of potential cannot be very large and hence the *C.D.*-anode potential curve should be of the type *A* in Fig. 35 ; this curve was obtained for a mercury anode in 0.66*N*-mercurous nitrate and 0.1*N*-nitric acid at 23°.* Similar behaviour is found with lead and silver in solutions of their nitrates ; the small polarization

* See Le Blanc, *Abh. Bunsen-Ges.*, 1910, 3.

which occurs in these cases can be reduced by stirring the solution or raising the temperature. Zinc, copper and cadmium anodes polarize slightly more than would be expected from concentration changes alone (curve *B*, Fig. 35, for a copper anode in *N*-copper sulphate and 3*N*-sulphuric acid), but the increase of potential is not considerable. The nature of the anions present has some influence on the results.* Anodes of iron, cobalt and nickel, however, show a marked polarization which can only be ascribed to an irreversibility in the ionization process. The variation of anode potential with *C.D.* for a nickel electrode in *N*-nickel chloride solution is shown in Fig. 36 for 16° and 52°; † the polarization is considerable even at low *C.D.*'s, as the reversible potential is about -0.24 volt. Increase of temperature reduces the polarization, since it presumably increases the velocity of a slow stage in the ionization process. It has been suggested that anodic dissolution

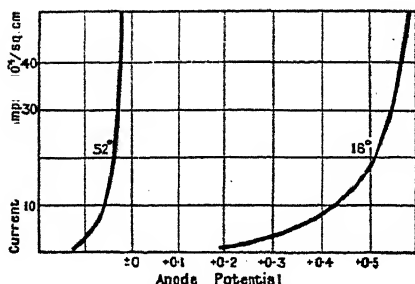


FIG. 36.—Anode Potentials of nickel at 16° and 52°

can only occur at certain active centres, and consequently appreciable polarization results.‡

In all the examples considered, and with tin, bismuth, antimony and the iron group metals at low *C.D.*'s, the efficiency for metal dissolution is 100 per cent., that is, in complete accord with the requirements of Faraday's laws. In the anodic dissolution of a metal like zinc, with one valency stage, there is no doubt as to the nature of the ions; but with copper, mercury, tin, lead, iron and gold the metal may dissolve as two different ions. It has been shown (p. 353) that when such a metal is placed into a solution of its ions, equilibrium is not reached until the potential of the metal is the same with respect to each type of ion; the concentrations (or activities) of the two ions are then in a definite ratio to one

* Müller (E.) and Barchmann, *Z. Elektrochem.*, 1933, 39, 341.

† Schoch, *Amer. Chem. J.*, 1909, 41, 208; Schweitzer, *Z. Elektrochem.*, 1910, 15, 606.

‡ Georgi, *ibid.*, 1932, 38, 681, 714; 1933, 39, 209, 736, 745.

another. If the metal is made an anode in the solution it will dissolve and maintain the equilibrium; hence it must form the two ions in amounts proportional to the equilibrium concentrations. Consider the behaviour of the metal iron:

$$\pi_{\text{Fe}, \text{Fe}^{2+}} = -0.44; \quad \pi_{\text{Fe}^{2+}, \text{Fe}^{3+}} = 0.77; \quad \pi_{\text{Fe}, \text{Fe}^{3+}} = -0.04;$$

equilibrium is reached when

$$-0.44 + 0.058 \log [\text{Fe}^{2+}] = -0.04 + 0.058 \log [\text{Fe}^{3+}],$$

that is when $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ is about $10^{6.9}$. An iron anode will, therefore, dissolve to form ferrous and ferric ions in this proportion; the former will be produced in greatly predominating amount, and the iron will appear to dissolve entirely in the bivalent (ferrous) form. In a solution containing initially neither ferrous nor ferric ions an iron anode will dissolve right from the commencement in the equilibrium ratio. Similarly it may be shown, in agreement with experiment, that tin dissolves mainly in the lower valency condition in acids and neutral salt solutions, and that lead forms plumbous ions almost exclusively in hydrochloric and silicofluoric acids, and in alkali solutions.* With copper, however, dissolution occurs mainly in the higher valency (cupric) state. The standard potentials for copper-cuprous ions and copper-cupric ions are about $+0.52$ and $+0.34$ respectively; hence a solution that is in equilibrium with metallic copper must contain cupric and cuprous ions in the ratio given by $[\text{Cu}^{2+}]/[\text{Cu}^{+}]^2 = 10^{6.2}$.† A copper anode will dissolve, therefore, almost entirely in the cupric condition; a very small quantity of the metal does enter the solution as cuprous ions, in order to maintain the necessary equilibrium.‡ Any factor which tends to reduce the concentration of either ion will cause the anode to dissolve preferentially in that particular form; for example, if the cuprous ions are oxidized to cupric by means of a current of air the copper anode will tend to dissolve as cuprous ions so as to re-establish equilibrium. In an alkali cyanide solution copper dissolves almost completely in the univalent form, since the concentration of the cuprous ions is kept at an extremely small value by the formation of a cuprocyanide complex. Even in hydrobromic, and to some extent in concentrated hydrochloric, acid the formation of cuprous complexes will result in the anode

* Elbs *et al.*, *ibid.*, 1902, 8, 760; 1903, 9, 781; 1904, 10, 364.

† Cf. Heinerth, *ibid.*, 1931, 37, 61.

‡ See, however, Essin, *Z. physikal. Chem.*, 1931, 156, 41, who explains the formation of 'anode mud' on the basis of the assumption that the anode dissolves to form the two ions in amounts directly proportional to their concentrations.

dissolving partly as bivalent and partly as univalent ions.* Mercury is an interesting example; the normal potentials are $+0.80$ and $+0.86$ for mercuric and mercurous ions respectively, and at equilibrium the ratio $[\text{Hg}_2^{2+}]/[\text{Hg}^{+}]$ is about 120.† A mercury anode will dissolve in a nitrate solution, in which complex ions are not formed, in the ratio of 120 mercurous (Hg_2^{2+}) ions to one mercuric ion. If a concentrated solution of potassium iodide, or of cyanide, is used as electrolyte, the mercuric ions are removed in the form of complexes, HgI_4^{2-} and $\text{Hg}(\text{CN})_4^{2-}$ respectively, and dissolution occurs in the bivalent state. It may be noted here that exactly the same considerations as developed for the dissolution of a metal may be applied to the study of the deposition of a metal capable of existing in two, or more, valency conditions.

Anodic Dissolution of an Alloy ‡—The anodic behaviour of an alloy of two metals depends on the variation of electrode potential with composition; in this connection the structure of the alloy must be considered. The metals may be completely immiscible in the solid state, or they may be completely or partially miscible, forming one or more series of solid solutions respectively; the metals may also form compounds and these may be miscible with either of the pure metals. If the potential is measured in a solution on which the alloy has no action, e.g. a solution of a salt of the baser metal, it is generally found that as long as two phases are present the potential of the alloy is equal to that of the baser phase. When the two metals do not unite chemically, nor are appreciably miscible with one another, the same two phases are always present, and the electrode potential remains constant and equal to that of the less noble constituent; if the alloy only contains a very small proportion of the latter metal the potential frequently rises to that of the more noble metal. If a continuous series of solid solutions is formed the electrode potential might be expected to vary continuously with the composition of the alloy; this is, however, frequently not the case, since the more noble metal exerts a protective effect on the other,§ and up to a certain concentration of the latter the potential of the alloy is the same as that of the nobler metal. Beyond this concentration the potential falls rapidly and is almost equal in value to that of the baser metal.

* Cf. Müller (W. J.), *Z. Elektrochem.*, 1935, **41**, 774.

† Ogg, *Z. physikal. Chem.*, 1898, **27**, 293; Abel, *Z. anorg. Chem.*, 1901, **26**, 375.

‡ Foerster, *Elektrochemie wässriger Lösungen*, 1922, p. 400; Allmand and Ellingham, *Applied Electrochemistry*, 1924, p. 127; Guertler, *Metallographie*, Part II, Vol. I (III), p. 43 (Kremann).

§ Tammann, *Z. anorg. Chem.*, 1919, **107**, 1; see also, Le Blanc *et al.*, *Ann. Physik*, 1928, **86**, 929; Tammann, *ibid.*, 1929, **1**, 309, 321; Le Blanc *et al.*, *ibid.*, p. 318; Kröger, *Z. anorg. Chem.*, 1929, **179**, 27.

When two metals have a limited solubility in one another two solid solutions are possible ; as long as only one is present the potential generally varies with the composition, but it remains constant when both solid solutions are present, irrespective of their relative amounts. Should compound formation occur the electrode potential will remain equal to that of the less noble metal until sufficient of the other is present for the alloy to consist entirely of the compound ; the potential then rises to the value for the compound and remains there as long as the phases are compound and noble metal. If a second compound is formed as the amount of the latter is increased there is a further rise in potential when its composition is attained ; finally the value rises to that of the more noble metal when the alloy consists almost entirely of that constituent. If the compound forms a solid solution with the noble metal then the potential, after rising suddenly when the composition of the compound is reached, increases gradually towards that of the nobler metal as its proportion is increased.

When used as an anode the least noble phase, that is the one with the more negative potential against the electrolyte used, dissolves first ; the potential remains constant, apart from concentration and other polarization, until this phase has disappeared. The subsequent change of potential depends on the nature of the remaining phase. If a solid solution is present the metals will dissolve simultaneously, since the electrode consists of one phase ; the anode potential depends on the composition of the alloy, and on the protective effect, if any, of the more noble constituent. Where the anode consists of two phases, the noble one left undissolved may form a coating over the electrode and prevent the dissolution of the baser phase ; the anode potential will then rise, the coating will dissolve and the potential may fall again as the less noble phase is exposed. In a coarse-grained alloy this mechanical protective effect cannot arise, but in these circumstances the dissolution of one constituent may cause the electrode to disintegrate. In electrolytic refining of metals an effect of this kind is responsible for a large proportion of the ' anode mud ' containing the noble impurities present in the original anode. A pure metal electrode may consist of large crystals held together by finely divided material ; the latter will have the more negative potential and so dissolves more readily, thus frequently causing disintegration of the anode of a single metal.

Passivity *—Although a nickel anode is considerably polarized

* See Heathcote, *J. Soc. Chem. Ind.*, 1907, 26, 899 ; Gerding and Karssen, *Z. Elektrochem.*, 1925, 31, 135 ; Evans (U.R.), *Nature*, 1931, 128, 1062 ; for literature summaries. For references to recent work, see Hedges, *Ann. Reports Chem. Soc.*, 1934, 31, 127.

even at low *C.D.*'s it still dissolves quantitatively according to the requirements of Faraday's laws. If the *C.D.* is increased, however, a point is reached at which the anode potential rises suddenly, and there is a corresponding decrease of current; at the same time it is found that the nickel anode has ceased to dissolve, although its appearance is unchanged. The metal is then said to be **passive**. The general nature of the potential changes is shown in Fig. 37; *AB* represents the variation of anode potential with *C.D.* whilst the electrode is 'active' and dissolves quantitatively. At *B* the electrode becomes passive and the potential increases whilst the current decreases to the condition represented by *C*; * if the *C.D.* is further increased the anode potential rises rapidly until a new process, generally oxygen evolution at *D*, commences and then

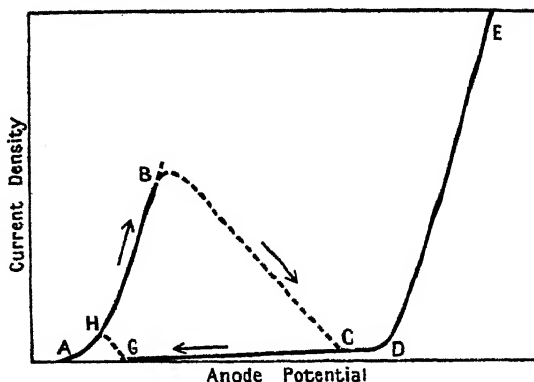


FIG. 37.—Anode potential-current density curves for the onset of passivity

considerable current can flow with little further polarization (*DE*). Along *CE* the nickel anode has almost, although not entirely, ceased to dissolve.† When the *C.D.* is decreased from *E* the active condition is not regained at *C*, but the current must be reduced to a much lower value (*G*) before the potential falls suddenly to *H*, and quantitative nickel dissolution recommences. If the current is switched off whilst the electrode is passive it returns slowly to the active condition on standing; by using the passive metal as cathode in a cell, or by touching it with a less noble metal under the surface of an electrolyte, or by scratching the surface, the active state is rapidly regained. The attainment of passivity depends on the nature of the electrolyte; a nickel anode becomes passive at

* Fredenhagen, *Z. physikal. Chem.*, 1903, 43, 1; Schoch and Randolph, *J. Physical Chem.*, 1910, 14, 719.

† Flade, *Z. physikal. Chem.*, 1911, 76, 513; White, *J. Physical Chem.*, 1911, 15, 768; Lobry de Bruyn, *Rec. trav. chim.*, 1921, 40, 53.

a lower *C.D.* in alkaline than in acid solution.* The presence of chlorine ions markedly inhibits the onset of the passive state, but oxidizing anions, e.g. iodate, bromate, chlorate, chromate and nitrate, favour it; other anions also have a specific influence.† Increase of temperature decreases anodic polarization and a higher *C.D.* is required to cause the anode to become passive. The actual *C.D.* at which an electrode passivates depends on the conditions of electrolysis (see p. 488).‡

Although a nickel anode has been discussed the general behaviour described is typical also for iron and cobalt; § iron is, however, much more difficult to render passive than is nickel, whereas cobalt probably occupies an intermediate position. A chromium anode exhibits somewhat different behaviour; || although the metal dissolves at first to form chromous ions and then becomes passive as the *C.D.* is increased, dissolution does not cease. The potential rises rapidly to about +1.1 volt, but instead of the evolution of oxygen occurring, a preferential process, namely the formation of Cr^{+++} ions takes place; these come to equilibrium with the hydroxyl ions in solution:



with the result that the chromium anode continues to dissolve as *chromate*. If the solution contains iodine ions, however, the discharge of these can occur at a lower potential (+0.6 volt) than the formation of the hexavalent ions; hence the metal will cease to dissolve when passive but iodine will be liberated. Chromium is more readily passivated in alkaline than in acid solution; temperature has a marked inhibitive effect, but chlorine ions do not appear to be so effective in preventing passivity as with the iron group metals. The metal retains its passivity for some time after use as an anode; it may be placed in a solution of acid and remain as inert as platinum, although in the active condition its standard potential is about -0.48 volt. By making passive chromium a cathode in an electrolytic cell, however, the active condition is rapidly regained. Although oxidizing agents generally favour passivity, the behaviour of a tin anode appears to be exceptional in

* A nickel anode may be used in a gas coulometer containing alkali.

† Schoch, *Trans. Faraday Soc.*, 1914, 9, 274; Georgi, *loc. cit.*

‡ See also Flade, *loc. cit.*; Byers *et al.*, *J. Amer. Chem. Soc.*, 1914, 36, 2004; 1919, 41, 1902.

§ Iron: Schönbein (introduced the term 'passivity'), *Ann. Physik*, 1836, 37, 390; 38, 444; 39, 342; 1837, 41, 53; 1838, 43, 103; Hittorf, *Z. physikal. Chem.*, 1900, 34, 385, etc.; Cobalt: Byers, *J. Amer. Chem. Soc.*, 1908, 30, 1728; Byers and Thing, *ibid.*, 1919, 41, 1902.

|| Hittorf, *Z. physikal. Chem.*, 1898, 25, 729; 1899, 30, 481; 1900, 34, 385; *Z. Elektrochem.*, 1898, 4, 482; 1899, 6, 6; 1900, 7, 168; Grube *et al.*, *ibid.*, 1926, 32, 70; Müller (E.) and Essin, *ibid.*, 1930, 36, 963.

this respect; it can be made passive quite readily in sulphuric and the simple halogen acids, but not in nitric, iodic and perchloric acid solutions. Incidentally, chlorine ions do not appear to prevent the passivity of tin.* Molybdenum and tungsten are rendered passive more readily in acid than in alkaline solution; passivity, therefore, depends both on the metal and the electrolyte.

Platinum and gold are generally regarded as unattackable electrodes, but this is because they are nearly always passive. A gold anode dissolves in neutral or acid chloride solutions at very low *C.D.*'s to form Au^{+++} ions at a potential of +1.2 to +1.3 volt; as the *C.D.* is increased the electrode becomes passive, ceases to dissolve and chlorine is evolved at +1.7 to +1.8 volt. By increasing the acidity or raising the temperature it is possible to retard the onset of passivity to high *C.D.*'s.† Platinum, although less noble than gold, is more easily made passive; small quantities do, however, dissolve from a platinum anode in sulphuric acid and are found in the electrolyte.‡ In oxy-acids passivity sets in so rapidly that the quantity of platinum dissolved at the anode is very minute, but in ammoniacal solutions§ or in hydrochloric acid, especially if the platinum is finely divided, the anodic attack is much greater.

The phenomena of anodic passivity are of importance in electrolytic refining and plating, since the impure metal is just as liable as the pure form to become passive; if this occurs, not only is the bath voltage increased, but the solution becomes depleted of metal ions. With nickel passivity may be avoided by using a high temperature and adding chlorides to the electrolysis bath; these measures are, however, not effective for a gold anode. An alternating current is then superposed on to the direct electrolysis current; this has the general effect of retarding the onset of anodic passivity, and can even cause the dissolution of a platinum anode.||

'Mechanical' Passivity—In all the cases discussed the pas-

* Steinherz, *ibid.*, 1924, 30, 279.

† Wohlwill, *ibid.*, 1898, 4, 381; Coehn and Jacobsen, *Z. anorg. Chem.*, 1907, 55, 321; Shutt and Walton, *Trans. Faraday Soc.*, 1932, 28, 740; 1933, 29, 1209; 1934, 30, 914; 1935, 31, 636; Armstrong and Butler, *ibid.*, 1934, 30, 1173.

‡ Senter, *ibid.*, 1906, 2, 142; Marie, *Compt. rend.*, 1907, 145, 117; 1908, 146, 475; Ruer, *Z. Elektrochem.*, 1908, 14, 309, 633; see also Tafel, *Z. physikal. Chem.*, 1905, 52, 349.

§ Thiel, *Z. Elektrochem.*, 1908, 14, 204.

|| Ruer, *Z. physikal. Chem.*, 1903, 44, 81; Brochet and Petit, *Z. Elektrochem.*, 1904, 10, 909; 1905, 11, 441; Wohlwill, *ibid.*, 1910, 16, 25; Grube and Gmelin, *ibid.*, 1920, 26, 153; Grube, *ibid.*, 1922, 28, 275; Kohlschütter and Schödl, *Helv. Chim. Acta*, 1922, 5, 490; Allmand and Puri, *Trans. Faraday Soc.*, 1925, 21, 1; Tucker and Loesch, *Ind. Eng. Chem.*, 1917, 9, 841, use A.C. for nickel anodes.

sive anode appears as bright as the active metal, but in many instances the simplest anodic processes are prevented by the production of a visible, insoluble film on the metal surface; this has been called 'mechanical' passivity, as distinct from 'electrochemical' passivity,* although, as will be seen subsequently, it is doubtful if there is any fundamental difference between the two types. When the cations formed by the dissolving anode can form a sparingly soluble compound with the anions of the electrolyte, the electrode process may be considerably altered. If the substance adheres to the anode in the form of a badly conducting film which increases in thickness, the dissolution of the metal is impossible, but discharge of anions may be possible at high voltages; this type of case in the extreme leads to 'valve action', which will be considered later (p. 498). Generally the film is not continuous and adherent, but merely has the effect of decreasing the exposed surface of the electrode to a considerable extent; the actual *C.D.* is thus increased and the anodic polarization may increase sufficiently to allow another process to occur. These are probably the conditions with a lead anode in sulphuric acid; the plumbous ions unite with the SO_4^{--} ions to form a loose film over the metal. The *C.D.* is increased so much that the original process cannot occur sufficiently rapidly to maintain the current; hence the potential rises until another process, $\text{Pb} \rightarrow \text{Pb}^{+++} + 4e$, occurs. If the acid is concentrated (s.g. > 1.7) the lead enters solution and forms plumbic sulphate which may be crystallized out,† but in more dilute solutions lead dioxide is precipitated and tends to close up the free space on the anode. This new film is, however, a good conductor, and so, although no lead ions go into solution, anions can be discharged at it; the potential, therefore, rises further and oxygen evolution occurs. If the lead sulphate film can be prevented from adhering at all to the anode the metal will continue to dissolve in the bivalent condition; this may be achieved by adding a chlorate or nitrate to the sulphuric acid or sulphate solution.‡ Thallium, antimony and bismuth also form sparingly soluble sulphate films when used as anodes in sulphuric acid solution, and so 'mechanical' passivity is produced, leading eventually to oxygen evolution.§ In alkaline solution most metals tend to form films as their hydroxides are insoluble; anodes of iron, cobalt,

* See Foerster, *op. cit.*, pp. 230, 415; also Müller (W. J.), *Z. Elektrochem.*, 1934, 40, 578.

† Elbs and Fischer (F.), *ibid.*, 1900, 7, 343; Elbs and Nübling, *ibid.*, 1903, 9, 776.

‡ Luckow, *ibid.*, 1897, 3, 482; Le Blanc *et al.*, *ibid.*, 1902, 8, 255.

§ Müller (W. J.), *ibid.*, 1909, 15, 696; see also Hedges, *J. Chem. Soc.*, 1926, 2580, 2878.

manganese and lead dissolve at first in concentrated alkali as bivalent ions, which then form complex anions (e.g. FeO_2^{--} , HPbO_2^-). After a time the solution near the anode becomes saturated with metal hydroxide, and the latter begins to cover the electrode; the potential rises and a dark film (e.g. Fe_3O_4 , PbO_2) is then formed.* Since these oxides are conductors, anion discharge may occur, although cation formation is prevented, and after another increase of potential oxygen evolution commences. Somewhat similar phenomena occur with thallium, zinc, tin and copper anodes in alkaline electrolytes.† The presence of chlorides in an alkaline solution generally prevents adhesion of the oxide film to the anode and the metal continues to dissolve; the mechanism of the action of chlorine ions in this respect is obscure.‡

Chemical Passivity—This condition, although closely related to ‘electrochemical’ passivity, is produced without the aid of polarization; if iron is dipped into strong nitric acid there may be an instantaneous reaction, but the metal does not continue to dissolve. Although the resulting metal appears unchanged, it is insoluble in dilute acids and will not replace metallic silver from solution; the iron has thus become a noble metal, but scratching the surface or touching it with a piece of active iron under the surface of an electrolyte, causes it to lose its nobility.§ These phenomena, discovered in 1790, were forgotten for many years, but were re-discovered by Wetzlar in 1827|| and investigated by Schönbein, Faraday and others.** It was found that in general oxidizing agents, e.g. nitric acid (s.g. > 1.25), nitrates, iodic, chloric and arsenic acids, chromates and permanganates, could induce passivity not only in iron, but also in cobalt, nickel and chromium. By heating in air these metals could also be rendered passive; and a semi-passive condition, in which the electrode potential was

* Glasstone, *ibid.*, 1922, 121, 2091; Grube, *Z. Elektrochem.*, 1927, 33, 389.

† Müller (W. J.), *loc. cit.*; Goldschmidt and Eckardt, *Z. physikal. Chem.*, 1906, 56, 389; Müller (E.), *Z. Elektrochem.*, 1907, 13, 133.

‡ Evans, *Trans. Faraday Soc.*, 1922, 18, 1; *J. Chem. Soc.*, 1927, 1020.

§ Keir, *Phil. Trans.*, 1790, 80, 374.

|| Schweigger's *J. Chemie Physik*, 1827, 49, 470; 50, 88, 129; 56, 206; Herschel, *Ann. Chim. Phys.*, 1833, 54, 87, claimed to have made the same discoveries in 1825.

** Schönbein, *loc. cit.*; *Phil. Mag.*, 1836, 9, 53; 1837, 10, 174; Faraday, *ibid.*, 1836, 9, 61; *Experimental Researches in Electricity*, Everyman Edn., p. 317 *et seq.*; Heathcote, *loc. cit.* (for early history); Gerding and Karssen, *loc. cit.*; Senter, *Trans. Faraday Soc.*, 1914, 9, 203; Bennett and Burnham, *Trans. Amer. Electrochem. Soc.*, 1916, 29, 217; *J. Physical Chem.*, 1917, 21, 107; Evans (U. R.), *J. Chem. Soc.*, 1930, 478; 1932, 2476; *Nature*, 1931, 128, 1062; Cone and Tartar, *J. Amer. Chem. Soc.*, 1934, 56, 48.

intermediate between passive and active states, could be induced in iron, cobalt, nickel, chromium, molybdenum, tungsten, vanadium and ruthenium by mere exposure to air.* Contact in almost any solution with a more noble metal causes an iron-group metal to become passive, since the combination consists of a short-circuited cell in which the iron is the anode. In the passive condition iron is almost as noble as platinum; scratching the surface causes the formation of internal voltaic cells in which the passive iron is the cathode. The latter then becomes active and this activity spreads over the whole of the metal. Contact with a less noble metal has the same effect, and so also has cathodic polarization; if the electrolyte used in any of these cases is a strong oxidizing agent passivity may set in again. Passive iron becomes active on standing in water (Keir) and more rapidly if placed in acid solutions (Schönbein) or solutions containing halogen ions; the rate at which activity is regained may be accelerated by heating the solution. For this reason the concentration of nitric acid required to cause iron to become passive increases as the temperature is raised.† In general the resemblance between electrochemical and chemical passivity is so great, that there is some justification for treating them as identical.

Theories of Passivity ‡—In view of the large number of observations, many of them conflicting, made in connection with passivity it is not surprising that many theories have been proposed, from time to time, to account for them. At first sight a single comprehensive theory of passivity would appear impossible, but in spite of this it seems that such a theory is being gradually evolved. The first definite views on passivity were those of Faraday; he suggested that the surface of a passive metal was oxidized, or that the atoms of the 'metal were in such a relation to the oxygen of the electrolyte as to be equivalent to an oxidation'; the metal atoms which had 'their affinity for oxygen satisfied' had no tendency to be attacked by acids. Faraday realized that the oxide layer might be so thin as to be invisible. This theory held its ground until Hittorf showed by his work on chromium that it had to face considerable difficulties, and that the properties of an oxide responsible for passivity would need to be different from those of any known oxides of the metal. Other authors considered that a definite oxide could not be present, as the electrode potential of

* Muthmann and Frauenberger, *Sitzungsber. Bayer. Akad. Wiss.*, 1904, 34, 201; *Z. Elektrochem.*, 1904, 10, 929, for summary.

† Hedges, *J. Chem. Soc.*, 1928, 969.

‡ For reviews see Grave, *Jahrb. Radioak. Elektronik*, 1911, 8, 91; Discussions, *Trans. Faraday Soc.*, 1914, 9, 203; 1924, 19, 748; Allmand and Ellingham, *op. cit.*, p. 142; Hedges, *Ann. Reports*, 1934, 31, 127.

a passive metal varied over a wide range ; * this argument is not sound, however, for if the oxide formed a solid solution with the metal of the electrode the potential would depend on the concentration of this solution. Bennett and Burnham† have, in fact, considered passivity to be due to the formation of an unstable oxide which is adsorbed and so stabilized by the metal. The supposed identity in light-reflecting powers of anode and cathode‡ suggested that an oxide film could not be present on a passive metal, especially as a lead dioxide film 0.8×10^{-7} cm. in thickness produced a marked effect. In recent years, however, it has been shown that passive electrodes do *not* reflect plane polarized light to the same extent as do active electrodes ; hence films of some kind are probably present on the surface.§ In agreement with this is the fact that the photo-electric emission from passive iron is only about half that from active iron.|| The view that the surface of a passive metal is covered with an oxide film has also received support from other sources ; ** a concentrated solution of alkali, able to dissolve an oxide film, was found to render active an iron electrode which had been previously passive. It may be recalled, too, that molybdenum and tungsten, which form higher oxides of a definitely acidic nature, tend to remain active as anodes in alkaline solution, but become passive in acids.

By gentle anodic action or by means of iodine, Evans†† has succeeded in dissolving away the inner portion of iron electrodes made passive by anodic treatment, by the use of oxidizing agents, or by exposure to air ; in each case a very thin, transparent and almost colourless film of oxide was left after the basis metal was dissolved out. The film is quite invisible when attached to the metal, but can be seen when separated from it. Hedges‡‡ considers that an oxide film is also present at the surface of iron rendered passive by the action of nitric acid. Rapid rotation of passive iron in 86 per cent. nitric acid caused the metal to become active within thirty seconds ; the whirling motion evidently favoured the

* Fredenhagen, *Z. physikal. Chem.*, 1903, 43, 1 ; 1908, 63, 1 ; Muthmann and Frauenberger, *loc. cit.*

† *Loc. cit.*

‡ Müller (W. J.) and Königsberger, *Z. Elektrochem.*, 1907, 13, 659 ; 1909, 15, 742.

§ Freundlich, Patscheke and Zocher, *Z. physikal. Chem.*, 1927, 128, 321 ; 130, 289 ; Tronstad, *ibid.*, 1929, 142, 241 ; 1932, 158, 369 ; *Trans. Faraday Soc.*, 1933, 29, 502.

|| Allen, *ibid.*, 1914, 9, 247 ; Frese, *Z. wiss. Photo.*, 1921, 21, 37 ; see, however, Becker and Hilberg, *Z. Elektrochem.*, 1925, 31, 31.

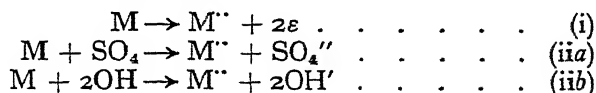
** Haber and Maitland, *ibid.*, 1907, 13, 309 ; Krassa, *ibid.*, 1909, 15, 490, 981 ; Grube and Feucht, *ibid.*, 1922, 28, 568 ; Goldmann and Ruff, *Z. physikal. Chem.*, 1930, B 8, 180.

†† *J. Chem. Soc.*, 1927, 1020.

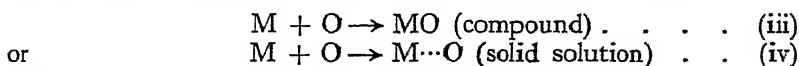
‡‡ *Ibid.*, 1928, 969.

removal of the oxide film. The question now arises as to the nature of this oxide, which is apparently insoluble in acids; for passive iron both Evans and Hedges consider it to be ferric oxide.* The former has shown that the oxide films, after removal from the basis metal, are only slowly soluble in acids, and the latter has found that ignited ferric oxide is almost insoluble in concentrated nitric acid at ordinary temperatures. Further, the ignited oxide commences to dissolve appreciably at the same temperature as passive iron becomes active in that particular nitric acid solution. Hence if it is assumed that the oxide is formed on the electrode in a compact, non-hydrated form, its insolubility in acids is not difficult to explain; there is thus no necessity to postulate the existence of abnormal oxides. It appears probable, therefore, that a passive electrode is covered with a thin, invisible film of oxide, generally of a high valency type since it is formed under oxidizing conditions.† Although the existence of an oxide film may be admitted it must be realized that the oxide may not be the *cause*, but merely the *consequence* of passivity. It is, therefore, necessary to discover why metal dissolution ceases, how the oxide film is formed, and whether it is necessary for the maintenance of passivity.

The exact mechanism of metal dissolution at an anode is uncertain, but the various possibilities are (for a bivalent metal):



$\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{O}$, or $2\text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$, then



followed by $\text{MO (or M}\cdots\text{O)} + 2\text{H}' \rightarrow \text{M}'' + \text{H}_2\text{O}$.

If the process responsible for metal dissolution occurs slowly polarization will result, and the anodic potential at increasing *C.D.*'s may rise to the value at which oxygen evolution is possible. Since metal dissolution then ceases almost entirely, the oxygen must either act as a negative catalyst for the processes involved in the change $\text{M} \rightarrow \text{M}''$, or it may remove a positive catalyst pre-

* Evans, *ibid.*, 1929, 2651, 1930, 1361; cf. also Benedicks and Sederholm, *Z. physikal. Chem.*, 1928, 138, 123; see, however, Bancroft and Porter, *J. Physikal. Chem.*, 1936, 40, 37, who suggest the oxide is FeO_3 .

† See also Müller (E.) and Spitzer, *Z. anorg. Chem.*, 1906, 50, 321; Ruer, *Z. Elektrochem.*, 1908, 14, 633; Dunstan and Hill (J. R.), *J. Chem. Soc.*, 1911, 99, 1853; Brown (J. G.), *J. Physical Chem.*, 1921, 25, 429; Isgarischev and Obtruscheva, *Z. Elektrochem.*, 1923, 29, 428; Liebreich and Wiederholt, *ibid.*, 1924, 30, 263; Grube, *ibid.*, 1927, 33, 389; cf., however, Krüger and Nährung, *Ann. Physik.* 1927, 84, 939.

viously present, or it may form a protective oxide film. Fredenhagen* considered that for metals which become passive readily process (iii) occurs slowly and so an 'oxygen charge' accumulates; when this 'charge' covers the whole surface the metal is passive. This theory assumes a slow reaction between a metal and atomic oxygen, whereas passivity sets in most readily with metals which are easily oxidized. In a modified theory† a metal-oxygen alloy, or solid solution, was supposed to form, and this was assumed to act as a negative catalyst for the ionization process (i).‡

Other authors§ favoured the view that pure iron is passive, but that it can be rendered active by hydrogen ions which catalyse process (i). Foerster|| originally adopted a similar point of view, but later** he altered it somewhat; since neither deposition nor dissolution of the iron-group metals occurs at the reversible potentials, it may be inferred that the reaction



occurs slowly in both directions. It was considered that hydrogen acts as a negative catalyst for the discharge of nickel and similar ions,†† and consequently it must also retard the reverse process of ionization and dissolution. The function of hydrogen as an activator, which it undoubtedly is, must then be ascribed to the removal of oxygen or oxides; these presumably have an even greater retarding influence on the ionization process.‡‡ The ideas are unnecessarily involved and are, in any case, based on an assumption of doubtful accuracy; slowness of ionization may, nevertheless, play some part in facilitating passivity.

Smits has emphasized the fact that in Foerster's theory oxygen and hydrogen are assumed to retard the heterogeneous process involving the reaction

metal (solid) \rightleftharpoons ions (in solution) + electrons,

but the former considers that heterogeneous equilibrium is estab-

* *Loc. cit.*

† Muthmann and Frauenberger, *loc. cit.*

‡ See also Jordis, *Z. Elektrochem.*, 1905, **11**, 787; Flade and Koch, *ibid.*, 1912, **18**, 335; Flade, *Z. physikal. Chem.*, 1911, **76**, 513; Flade and Koch, *ibid.*, 1914, **88**, 307; Flade, *ibid.*, p. 569; Schoch, *Trans. Faraday Soc.*, 1914, **9**, 274; Stapenhorst, *Z. physikal. Chem.*, 1917, **92**, 238; Strauss and Hinnüber, *Z. Elektrochem.*, 1928, **34**, 407; Hasebrink, *ibid.*, p. 819.

§ Grave, *Z. physikal. Chem.*, 1911, **77**, 513; Adler, *ibid.*, 1912, **80**, 835; Rathert, *ibid.*, 1914, **86**, 567; Schmidt (G. C.), *Trans. Faraday Soc.*, 1914, **9**, 257.

|| *Abh. Bunsen-Ges.*, 1909, No. 2.

** *Z. Elektrochem.*, 1916, **22**, 95.

†† This view is probably incorrect, see Glasstone, *J. Chem. Soc.*, 1926, 2887.

‡‡ See Foerster, *op. cit.*, pp. 227, 431.

lished rapidly; an alternative point of view, based on the 'theory of allotropy', has been proposed.* Smits suggested that the homogeneous or inner equilibrium between atoms, ions and electrons in the electrode itself, is only set up slowly; as a result of anodic dissolution, electrons and ions are withdrawn from the metal, but as they are not replaced immediately by the ionization of atoms, the metal becomes poorer in ions and electrons. According to the equations already quoted (p. 441) this means that the electrode potential becomes more positive and polarization results; the increased potential favours the liberation of oxygen which further retards the ionization process and the metal ceases to dissolve.†

It has been indicated by Tammann‡ that his observations on the electrode potentials of solid solutions (p. 476) may be applied to the interpretation of passivity phenomena. If it is imagined that oxygen atoms can occupy definite positions in the space lattice of a metal, and so exert a protective effect on the less noble atoms of iron, etc., then anodic passivity is explicable. The anode may contain an appreciable oxygen concentration and yet have a negative potential, but once a certain proportion is exceeded the metal will be completely protected from attack; its potential will then rise rapidly towards that of an oxygen electrode. One of the difficulties of this theory is that it would require the potential at which passivity sets in to be definite, and to vary in a definite manner with the hydroxyl ion concentration of the electrolyte; these requirements are by no means met in actual practice. The views of Tammann may be brought into line with some suggestions made by Schmidt;§ the latter considers that the passive state occurs in metals which are very hard and have a high surface tension, and that any process disturbing the surface tends to produce activity. Tammann noted that the protective effect of a noble element was more marked with alloys of high melting point, in which the atoms are not very mobile; increase of temperature, or any change causing a surface rearrangement, reduces the protective action. The parallelism with the observations of Schmidt is interesting; if it has any significance it would suggest that the

* Smits, *The Theory of Allotropy*, Eng. trans., 1922, Chap. VII; Smits and Aten, *Z. physikal. Chem.*, 1914, 88, 743; 1915, 90, 723; Smits, *Trans. Faraday Soc.*, 1924, 19, 772; *Z. Elektrochem.*, 1930, 36, 20.

† For other theories of passivity based on the slowness of reaction velocities, see Le Blanc, *ibid.*, 1900, 6, 472; *Trans. Faraday Soc.*, 1914, 9, 251; Sackur, *Z. Elektrochem.*, 1908, 14, 612; Reichstein, *ibid.*, 1911, 17, 699; 1913, 19, 672; 1924, 30, 238; *Trans. Faraday Soc.*, 1914, 9, 228.

‡ *Z. anorg. Chem.*, 1919, 107, 103; see Allmand and Ellingham, *Trans. Faraday Soc.*, 1924, 19, 748.

§ *Z. physikal. Chem.*, 1923, 106, 105.

oxygen in the surface is not present in a mobile form, and hence exists as an oxide. It must be realized, however, that even copper, and other soft metals, can be made passive under suitable conditions,* and so the theory of Schmidt, rendered plausible by the views of Tammann, encounters a serious obstacle.†

In recent years reaction velocity theories have been discarded, and there has developed a tendency to regard ionization and dissolution of a metal as instantaneous,‡ as it is possible to account for the phenomena of passivity without the assumption of retarded reactions. Since 1924 W. J. Müller and his co-workers§ have thrown much light on the onset of passivity, and on this point many writers now agree; || the question of the factors maintaining passivity is still, however, controversial. Using horizontal anodes, protected by means of a glass hood so that the product formed at the anode does not diffuse away, Müller has found that iron, nickel and chromium can be rendered passive in acid solution by the application of very small polarizing currents. It was considered at one time that a 'critical' anodic *C.D.* was necessary before passivity set in, but this is not the case; the length of time during which the current must be applied before the anode becomes passive increases as the *C.D.* decreases. In *N*-sulphuric acid iron becomes passive in 12.4 secs. at a *C.D.* of 289 milliamps. per sq. cm., but if the *C.D.* is reduced to 15 milliamps., the time required is about 848 secs. By preventing diffusion from the anode, passivity has been brought about at smaller *C.D.*'s than had previously been considered effective. If the solution is stirred, or the temperature raised, the time required for passivity to set in at any particular *C.D.* is increased; on the other hand, if the solution is previously saturated with the corresponding salt of the metal used as anode, passivity can be brought about much more readily.

These results suggest that a substance accumulates in the vicinity of the anode until the solution becomes saturated; then the solid separates out and deposits on the electrode. In several instances this deposit has been separated and identified as a known salt. A large part of the anode thus becomes shielded and the effective *C.D.* on the clear portions is much increased; this in-

* See Hedges, *loc. cit.*

† See also Hasebrink, *loc. cit.*

‡ See, however, Smits, *loc. cit.*

§ *Z. Elektrochem.*, 1924, 30, 401; 1927, 33, 401; for full references to end of 1934, see Hedges, *Ann. Reports*, 1934, 31, 129; see also, Müller *et al.*, *Z. Elektrochem.*, 1935, 41, 83, 641; *Monatsh.*, 1935, 66, 35; *Ber.*, 1935, 68, 989; *Trans. Faraday Soc.*, 1935, 31, 1291; *Bedeckungstheorie der Passivität der Metalle*, 1933. For summarizing lecture, see *Trans. Faraday Soc.*, 1931, 27, 737.

|| Evans, *Chem. and Ind.*, 1927, 46, 1219; Hedges, *loc. cit.*; Tronstad, *loc. cit.*

crease eventually leads to the onset of passivity. It has been observed * that immediately *before* the passivation of an anode a visible film appears on it, but this is thrown off, or dissolves, when the electrode actually becomes passive and oxygen is evolved; the electrode then appears quite clean. From his earlier work Müller concluded that a passive metal has no surface film, but it is prevented from dissolving by the fact that the very high *C.D.* existing just before passivity commences causes a transformation of the anode metal into another, more noble, modification which tends to dissolve in a higher valency state.† Later he obtained evidence for the presence of oxide films,‡ and has accepted a theory similar in general lines to that considered below.

The mechanism proposed by Hedges § to account for the onset of passivity and the formation of invisible oxide films has the support of Evans || and appears to clarify the position in many ways; it is given here in a somewhat modified form. In the vicinity of an active anode in acid solution there will be a tendency for metal ions to accumulate, as a result of dissolution from the anode; in addition there will be an increase of hydroxyl ion concentration, as hydrogen ions migrate away. If the *C.D.* is increased this accumulation will result in the separation, depending on the acidity of the solution, of a normal or basic salt of the metal on the electrode surface; the film so formed is probably discontinuous and still allows the passage of metal ions into solution. The saturation of the liquid in the vicinity of the anode will thus continue, and more basic salt separates until the film becomes relatively thick and covers most of the electrode. This is presumably the film observed by Müller and by Hedges. The effective *C.D.* at the uncovered portions of the electrode will be very large, and the potential rises until hydroxyl ion discharge can occur; these discharged ions react with the metal and produce an adherent invisible film of oxide beneath the visible, thick but discontinuous layer.** The oxide film spreads rapidly across the electrode, and when it is covered, oxygen evolution commences, perhaps through the inter-

* Müller, *Z. Elektrochem.*, 1924, **30**, 241; Hedges, *J. Chem. Soc.*, 1926, 2878.

† Finkelstein, *Z. physikal. Chem.*, 1902, **39**, 91; Müller, *ibid.*, 1904, **48**, 577; *Z. Elektrochem.*, 1904, **10**, 832; Russell, *Nature*, 1925, **115**, 455; 1926, **117**, 47; *J. Chem. Soc.*, 1926, 1877; Sborgi, *Gazz. chim. Ital.*, 1926, **56**, 532; Lansing, *Phys. Rev.*, 1927, **29**, 216; Foerster and Krüger, *Z. Elektrochem.*, 1927, **33**, 406; Yamasaki, *J. Chem. Soc. (Japan)*, 1922, **43**, 655; Müller (R.), *Z. Elektrochem.*, 1929, **35**, 459.

‡ See, for example, Müller (W. J.) and Löw, *ibid.*, 1933, **39**, 872.

§ *J. Chem. Soc.*, 1928, 969. || *Ibid.*, 1929, 109; 1930, 478.

** The formation of the visible film is called 'Bedeckungspassivität', by W. J. Müller, whereas the production of the invisible layer is referred to as 'chemische Passivität'.

mediate formation of a higher oxide (p. 495). The evolution of gas causes the first film to be thrown off from the electrode surface, leaving the latter apparently clean; this discontinuous film has played its part in reducing the effective *C.D.* and is not necessary for the maintenance of passivity. Since the invisible oxide film, which is the one isolated by Evans, is adherent and continuous, it does not permit the passage of metal ions; hence it cannot increase in thickness and so remains invisible. Further, as it is apparently only slightly soluble in acids, it protects the surface of the anode completely and prevents any appreciable dissolution; if small portions should dissolve, as they undoubtedly do, they are immediately re-formed. Müller's view differs from that just given in ascribing the formation of the invisible film to an electronic change in the metal with the result that it dissolves in a higher valency state: the oxide film is then formed by the hydrolysis of the resulting salt. It is doubtful, however, whether an oxide or hydroxide precipitated in this manner would be so strongly adherent.*

The passivating action of nitric acid on iron can also be brought into line with the theory; in the vicinity of the metal, as dissolution proceeds, there is a large concentration of ferric and nitrate ions, but the hydrogen ion concentration is reduced. Ferric oxide, or a basic salt, may thus be thrown out of solution in the form of a thin adherent film which protects the metal from further attack; this film is probably not markedly attacked by nitric acid below 75°.† Rapid rotation of the passive metal helps the loosening of the film and the metal becomes, and remains, active. For metals capable of forming a thin adherent oxide layer, the passivity produced by chromate solutions or by exposure to air is readily understood. Reference has been already made to the anodic passivity of gold in halide solutions: here also there is evidence that a very thin oxide film is present on the electrode.‡ In this case the onset of passivity may be influenced by the limiting rate of diffusion of chlorine ions to the anode.§

According to these views the ease with which a metal may be made passive depends in the first place on the possibility of saturating the solution in the vicinity of the anode with a normal or basic salt or oxide. Iron, nickel, cobalt, chromium and other metals are thus easily made passive in dilute alkaline solutions. For the same reason lead readily becomes passive in sulphuric acid, owing to the formation of lead sulphate, but in alkaline solution passivity does not set in so easily as the monoxide is soluble. Lowering the temperature should favour passivity, and this it un-

* Cf. Shutt and Walton, *Trans. Faraday Soc.*, 1934, **32**, 914.

† Hedges, *loc. cit.*

‡ Shutt and Walton, *loc. cit.*

§ Armstrong and Butler, *loc. cit.*

doubtedly does; raising the temperature favours both increase of solubility and of diffusion from the anode and so inhibits the onset of passivity. Cobalt and copper dissolve vigorously in concentrated nitric acid at ordinary temperatures, but become passive at -11° ; even zinc and magnesium show signs of passivity at this temperature.* These observations suggest that passivity is a general property of most metals, exhibited under different conditions, however, depending on the nature of the metal, its salts and oxides, and on the electrolyte in which it is placed.

The visibility of the oxide film on a passive metal is connected with its porosity, solubility and adherence; a continuous, adherent film which is sparingly soluble, e.g. ferric oxide, does not increase in thickness once it has formed, and so remains invisible. A poorly adherent, and hence porous, and partly soluble film, e.g. copper oxide produced by placing copper in concentrated nitric acid at -11° , grows in thickness, since it allows to some extent the passage of metal ions, and so becomes visible; lead dioxide films produced in alkali or in sulphuric acid solutions, are probably similar. Such films are not completely protective and generally allow the metal to dissolve to an appreciable extent. Chlorine ions are apparently able to penetrate certain films, e.g. ferric oxide, and render them porous and hence ineffective; the presence of chlorides thus retards the onset of the passivity of iron. If the metal does become passive, however, for example in alkaline solution, the oxide film is able to grow in thickness, since it is porous, and becomes visible if chlorine ions are present.† For similar reasons a nickel anode, although passive, still dissolves to a marked extent in solutions containing chlorides.‡

Some objection has been raised against the oxide-film theory of passivity, mainly because of observations on the activating effects of various anions and of their influence on the onset of passivity.§ It is doubtful, however, whether the arguments really undermine the basis of the theory, and the results can probably be interpreted in terms of it,|| possibly with some slight modifications dealing with the question of the permeability of the films by various anions. On the whole it may be concluded that the theory of passivity based on the prior formation of a saturated layer near the metal and the subsequent production of an oxide or other film, visible or invisible, depending on conditions, can embrace all types of

* Hedges, *loc. cit.*; *J. Chem. Soc.*, 1930, 561.

† Haber and Goldschmidt, *Z. Elektrochem.*, 1906, 12, 49.

‡ Foerster and Krüger, *ibid.*, 1927, 33, 406.

§ Müller (E.) *et al.*, *ibid.*, 1931, 37, 185; 1932, 38, 407; 1933, 39, 414, 791, 884; 1934, 40, 802; *Z. physikal. Chem.*, 1932, 159, 68; see also Georgi, *loc. cit.*

|| See Müller (W. J.), *Z. Elektrochem.*, 1933, 39, 880; 1935, 41, 83.

passivity; there is thus no need to distinguish, except for purposes of general classification, between mechanical, chemical and electrochemical passivity.*

Oxygen Evolution—After an electrode has become passive, oxygen evolution generally commences on increasing the *C.D.*; the potential at which this occurs, however, is invariably more positive than the reversible value. There is thus an overvoltage for oxygen evolution. Since the oxygen electrode is not reversible (p. 336) the theoretical potential is generally calculated from the hydrogen potential; the *E.M.F.* of the hydrogen-oxygen cell is taken as 1.22 volts in all electrolytes. On this basis the minimum overvoltages for oxygen evolution in *N*-alkali hydroxide, given in Table LXVI, have been determined from the observations of Coehn and Osaka.†

TABLE LXVI
OXYGEN OVERVOLTAGES IN *N*-POTASSIUM HYDROXIDE

Nickel	0.06	Silver	0.41
Cobalt	0.14	Cadmium	0.43
Platinized platinum	0.25	Palladium	0.43
Iron	0.25	Platinum (smooth)	0.45
Lead	0.31	Gold	0.53

Measurements of the potentials for oxygen evolution at definite *C.D.*'s have also been made, but it is difficult to obtain reproducible and reliable results.‡ One reason is that the potential of an anode generally increases as the time of polarization is prolonged: for example, the value for a platinized platinum anode was found to change from 1.70 to 2.01 volts in four hours when polarized in 2*N*-potassium hydroxide solution at a *C.D.* of 0.01 amp. per sq.

* It is impossible in this book to deal with the explanations for all observed passivity phenomena; but it is hoped that the reader will use the theories described to develop his own explanations. For references to periodic phenomena in connection with passivity, see Fechner, *Schweigger's J. Chemie Physik*, 1828, 53, 61, 129, 141; Herschel, *Ann. Chim. phys.*, 1833, 54, 87; *Ann. Physik*, 1834, 32, 211; Fredenhagen, *Z. physikal. Chem.*, 1903, 43, 32; Adler, *ibid.*, 1912, 80, 385; Smits and de Bruyn, see Smits, *Theory of Allotropy*, Eng. trans., 1922, p. 359; Hedges, *J. Chem. Soc.*, 1926, 1533, 2580, 2878; Foerster and Krüger, *Z. Elektrochem.*, 1927, 33, 406. For passivity phenomena in non-aqueous solutions, see Sborgi *et al.*, *Atti Ist. Veneto*, 1921, 80, 1033; *Nuovo Cim.*, 1921, 22, 151; *Atti R. Accad. Lincei*, 1925, 1, 315; 1927, 5, 571; *Gazzetta*, 1926, 56, 532; Eggert, *Z. Elektrochem.*, 1927, 33, 94.

† *Z. anorg. Chem.*, 1903, 34, 86; see also Caspari, *Z. physikal. Chem.*, 1899, 30, 89; Garrison and Lilly, *Trans. Amer. Electrochem. Soc.*, 1934, 65, 171.

‡ Foerster *et al.*, *Z. Elektrochem.*, 1902, 8, 527; 1904, 10, 74; Westhaver, *Z. physikal. Chem.*, 1905, 51, 65; Newbery, *J. Chem. Soc.*, 1916, 109, 1066; Knobel, Caplan and Eiseman, *Trans. Amer. Electrochem. Soc.*, 1923, 43, 55; Bowden, *Proc. Roy. Soc.*, 1929, 126 A, 107.

cm. A smooth platinum electrode increased its potential from 2.1 to 2.6 volts in the same time.* Similar changes have been observed with other anode materials. By using a solution of sulphuric acid saturated with oxygen, Bowden † claims that the overvoltage of a platinum anode may be expressed by the equation

$$\omega = a + b \log I,$$

where ω is the overvoltage at the C.D. represented by I , which was varied from 5×10^{-8} to 10^{-2} amp. per sq. cm. This equation is not only of the same form as that representing the variation of hydrogen overvoltage with C.D. (p. 428), but the value of b is said to be the same, viz. $2.3 \times 2RT/F$, over a range of temperatures. If this is correct it implies a resemblance between oxygen and hydrogen overvoltages which had not been previously realized: the observations should, however, be extended to other metals. From the results of Foerster ‡ it appears that the oxygen overvoltage at a smooth platinum anode decreases by about 2 millivolts per degree in 2*N*-sulphuric acid and by about twice that amount in 2*N*-potassium hydroxide. Bowden § considers, however, that as is the case with hydrogen, the temperature coefficient of overvoltage depends both on the temperature and on the actual value of the overvoltage, as indicated by equation (iii), p. 431; from his results with a smooth platinum electrode in an oxygen-saturated solution of 0.2*N*-sulphuric acid the decrease of potential is found to be about 3 millivolts per degree at constant C.D. Increase of pressure may bring about a small decrease of oxygen overvoltage.||

The presence of fluorides increases the potential for oxygen evolution in both acid and alkaline solutions at platinum, gold, silver and graphite anodes.** Superimposed alternating current is supposed to cause a decrease of overvoltage, but the significance of the results in the literature is doubtful.†† Certain radiations of short wavelength have been reported as having some influence on anodic overvoltages.‡‡ No reliable data are available concerning the effect of hydrogen ion concentration on the minimum overvoltage

* Foerster, *Z. physikal. Chem.*, 1909, 69, 236.

† *Loc. cit.*

‡ *Loc. cit.*

§ *Loc. cit.*

|| Cassel and Krumbein, *Z. physikal. Chem.*, 1935, 171, 70; Schischkin, *Z. Elektrochem.*, 1936, 42, 693.

** Isgarischev and Stepanov, *ibid.*, 1924, 30, 138; see also, Müller (E.), *ibid.*, 1904, 10, 780.

†† von Wartenberg and Archibald, *ibid.*, 1911, 17, 812; Reitlinger, *ibid.*, 1914, 20, 261; Grube and Dulk, *ibid.*, 1918, 24, 237; Glasstone, *J. Amer. Chem. Soc.*, 1925, 47, 940; see also, Glasstone and Reynolds, *Trans. Faraday Soc.*, 1932, 28, 582.

‡‡ Grube and Baumeister, *Z. Elektrochem.*, 1924, 30, 322; Bowden, *Trans. Faraday Soc.*, 1931, 27, 505; Duclaux, *Compt. rend.*, 1935, 200, 1838.

or that at a definite *C.D.*, nor is there any information on the influence of bathotonic substances.* The difficulty in the former case is that the various anions which must be present appear to affect the electrode potential, and in the latter case the added substances are oxidized at the anode.

From experiments on the charging and discharging, by making the electrode cathodic after having functioned as an anode, of platinum in sulphuric acid saturated with hydrogen and oxygen, it appears that at a potential of about 1 volt the oxygen on the electrode becomes attached in a special manner. This has been described either as the formation of the oxide PtO_2 ,† or as the completion of a layer of adsorbed oxygen ‡ on the anode surface: it is not easy to decide between these two interpretations of the results, but the fact that the length of the arrest observed on discharge depends on the time during which the electrode has acted as anode appears to favour the former point of view. It is not impossible that an adsorbed layer is formed first, but that it becomes slowly converted into a definite oxide by reaction with the surface atoms of platinum. At this stage there is no visible oxygen evolution, but on further charging the potential rises rapidly and in a linear manner with the quantity of electricity passed, until gas evolution commences at about 1.5 volts in acid solution. The capacity of the double layer formed during this stage is about 3×10^{-5} coulombs per volt per sq. cm.: this is somewhat greater than the value observed for a cathode (p. 433), and suggests that the oxygen dipoles have a somewhat smaller moment than those involving hydrogen.

There is evidence that anodes, even of noble metals, are covered with a layer of oxide when oxygen is evolved at high *C.D.*'s: these oxides generally contain more oxygen than those stable under normal conditions. The gradual fall of potential, after the current is switched off, of a platinum anode which has been in use for some time, with definite halts at certain points, suggests the presence of definite oxides on the electrode.§ If oxides can form at a platinum electrode merely by circulating oxygen around it (p. 336) it is not surprising that higher oxides can be produced by anodic polarization. Grube || found that the potential given by platinum in contact with the oxide PtO_2 in 2*N*-sulphuric acid was 1.5 volts and fell slowly; this value is almost identical with the anodic potential of platinum when oxygen evolution commences. The fall of poten-

* See, however, Lintern and Adam, *Trans. Faraday Soc.*, 1935, **31**, 564.

† Bowden, *Proc. Roy. Soc.*, 1929, **125** A, 446.

‡ Butler *et al.*, *ibid.*, 1932, **137** A, 604; 1933, **143** A, 89.

§ Lorenz *et al.*, *Z. Elektrochem.*, 1909, **15**, 206, 293, 349, 661.

|| *Ibid.*, 1910, **16**, 627; see also Jirsa, *Z. physikal. Chem.*, 1924, **113**, 241.

tial of the oxide electrode was parallel with that of a polarized platinum anode; thus it is possible that the high potential of the latter is due to the presence of the trioxide. Since higher potentials than 1.5 volts have been obtained it is not improbable that PtO_4 is also present. There is evidence from the discharge of palladium and rhodium anodes that oxides of a peroxidic nature are formed as a result of polarization.* A copper anode in alkali becomes covered with a yellow layer, consisting probably of Cu_2O_3 and CuO_2 , from which evolution of oxygen occurs with the resultant formation of cupric oxide.† The potential for oxygen evolution at a smooth nickel anode in alkali is almost the same as for one covered with nickelic oxide (Ni_2O_3); hence it is not improbable that an oxide at least as high as the sesquioxide is present on a nickel anode.‡ Oxygen evolution at a lead and a lead dioxide anode takes place at almost identical potentials. In the latter case the presence of a higher oxide is indicated by the slow fall of potential on self-discharge; whereas in the former, the appearance of a black film, which is probably not the dioxide, corresponds with oxygen evolution. It appears, therefore, that at both lead and lead dioxide anodes unstable higher oxides are formed.§

Until relatively recent times it was generally accepted that oxygen evolution at the anode only occurred through the intermediate formation of such unstable oxides, and that these were responsible for the anodic overvoltage. Although it seems definitely established that higher oxides are frequently present it is not certain by any means that they are the fundamental cause of overvoltage. It is possible that at relatively high *C.D.*'s the measured anode potential is actually that of an unstable oxide, formed by combination of the electrode material with active oxygen, but there still remains to be accounted for the fact that oxygen evolution does not commence at or near the reversible potential in the given electrolyte.

As was suggested in the case of hydrogen (p. 439), Bowden || considers that the oxygen dipoles must acquire a certain amount of energy before they can leave the surface and it is this which determines the overvoltage. The quantum mechanical treatment described by Gurney** in connection with the neutralization of hydrogen ions is supposed to apply equally to the discharge of hydroxyl ions, the overvoltage being due to the fact that the energy levels of electrons in these ions do not overlap the vacant

* Butler and Drever, *Trans. Faraday Soc.*, 1936, 32, 427.

† Müller (E.), *Z. anorg. Chem.*, 1907, 54, 417; *Z. Elektrochem.*, 1907, 13, 133.

‡ Foerster, *ibid.*, p. 414. § Glasstone, *J. Chem. Soc.*, 1922, 121, 2091.

|| *Proc. Roy. Soc.*, 1929, 126 A, 107

** *Ibid.*, 1931, 134 A, 137; see also, Butler and Armstrong, *ibid.*, 1932, 137 A, 604; *Trans. Faraday Soc.*, 1933, 29, 1261.

levels in the anode. It is doubtful whether these relatively simple points of view cover all the complexities connected with the evolution of oxygen at an anode. Another interpretation of overvoltage arises from the suggestion by Glasstone and Hickling* that discharge of hydroxyl ions leads to the irreversible formation of hydrogen peroxide, by combination of the radicals in pairs; the electrode potential would then be determined by the oxygen arising from the decomposition of the peroxide. The formation of an adsorbed layer, or of an oxide, and the linear increase of potential with the quantity of electricity passed can be readily correlated with this suggestion. The potential for oxygen evolution, and hence the overvoltage, might be determined by the catalytic effect of the anode material on the decomposition of hydrogen peroxide and by the oxides formed on the electrode surface.

Halogen Ion Discharge—Although most metals dissolve when used as anodes in solutions containing halogen ions, it is possible for these ions to be discharged at certain unattackable electrodes, e.g. platinum, iridium, graphite, magnetite. As a general rule, at very low *C.D.*'s, the liberation of halogen commences in the close vicinity of the reversible potential.† Appreciable currents will pass even before this value is reached because of the depolarizing action resulting from the solubility of the halogen in the electrolyte, and the formation of perhalide ions, e.g. Br_3^- . With a platinized platinum anode chlorine, bromine and iodine are discharged close to the reversible potential even at fairly large *C.D.*'s; even at a smooth platinum anode the overvoltage for chlorine and bromine evolution at low *C.D.*'s is much smaller than for oxygen and hydrogen. If the *C.D.* is increased, however, or alternatively if electrolysis is prolonged, the electrode potential rises relatively suddenly about 0.6 volt above the reversible value, that is to approximately 1.9 volts in *N*-hydrochloric acid. The change from the lower to the upper potential state takes place most readily with chlorides, less readily with bromides, and least of all with iodides; it occurs sooner the higher the *C.D.*, the lower the halide concentration in the electrolyte, and the less acid the solution; it is apparently not affected appreciably by stirring and so is not connected with concentration polarization.‡ The presence in the electrolyte of cata-

* See, for example, *J. Chem. Soc.*, 1932, 2345; also p. 511 *infra*.

† Caspari, *Z. physikal. Chem.*, 1899, 30, 89; see also Knobel, Caplan and Eisman, *Trans. Amer. Electrochem. Soc.*, 1923, 43, 55; Chang and Wick, *Z. physikal. Chem.*, 1935, 172, 448; and references given below.

‡ Müller (E.), *Z. Elektrochem.*, 1900, 6, 573; 1902, 8, 426; Luther and Brislee, *Z. physikal. Chem.*, 1903, 45, 216; Pfeleiderer, *ibid.*, 1909, 68, 49; Boericke, *Z. Elektrochem.*, 1905, 11, 71; Foerster and Yamasaki, *ibid.*, 1910, 16, 321; Herschel, *Diss.*, Leipzig, 1912 (see Grube, *Trans. Faraday Soc.*, 1913, 9, 224; Foerster, *Z. Elektrochem.*, 1916, 22, 85).

lysts for hydrogen peroxide decomposition, e.g. manganous or ferrous chlorides, precipitated silver, or animal charcoal, favours the onset of the higher potential. Normally, the rise of potential does not occur at a platinized platinum electrode, but if this is previously polarized anodically, or if hydrogen peroxide catalysts are present, the upper potential stage sets in quite readily.* Increase of temperature has been found to favour the rise of potential in some cases. It may be noted that at the higher potentials the gas evolved contains large proportions of oxygen.

The high potential stage observed in the electrolysis of halide solutions has often been referred to as a state of 'halogen overvoltage', but this term appears to be unjustified as the potentials are undoubtedly connected with oxygen evolution. There are, therefore, two separate problems, which have previously been confused, to be considered: there is firstly, the origin of the true, but small, halogen overvoltage observed in the low potential condition, and secondly, the cause of the relatively sudden rise to the upper stage. Since chlorine commences to be evolved at smooth platinum and at other anodes at potentials close to the reversible value, from solutions saturated with the gas,† explanations of the overvoltage based on an inhibition of the ionic neutralization stage appear to be ruled out: these incidentally require that the slope of the straight line representing the variation of overvoltage with the logarithm of the *C.D.* should be $2.3 \times 2RT/F$ (cf. p. 443), whereas it is actually about half this value.‡ There is a possibility that the stage $2Cl \rightarrow Cl_2$ may occur slowly,§ although there is no definite evidence for or against this point of view.

The rise of potential occurring during electrolysis has been attributed to the retardation of one of the intermediate steps, probably the combination of atoms, in the anodic formation of molecular halogen from the ions, brought about by an oxygen charge or by an oxide on the surface of the anode.|| Even at the reversible chlorine potential in a *N*-chloride solution (1.36 volt), hydroxyl ion discharge is theoretically possible, and the chlorine gas liberated actually contains a small proportion of oxygen. The less acid the solution the more readily will hydroxyl ion discharge occur, and so the polarization of halogen ion discharge should occur at lower *C.D.*'s. Since the reversible potentials of bromine and iodine are about 1.08 and 0.54 volt respectively, it is clear that these ions will be discharged in preference to hydroxyl ions, unless the solution is made neutral in the former instance, and alkaline

* Glasstone and Hickling, *J. Chem. Soc.*, 1934, 10.

† It is not certain if this applies to carbon anodes.

‡ Chang and Wick, *loc. cit.*

§ Foerster, *loc. cit.*

|| *Idem.*, *loc. cit.*; Grube, *loc. cit.*

in the latter. The theory proposed is thus in general agreement with the observations, but it does not account for the effect of catalysts for the decomposition of hydrogen peroxide, e.g. bone charcoal, nor for the surprising influence of temperature in favouring the onset of the upper potential stage in certain cases. In an alternative explanation * it is suggested that simultaneously with the reversible discharge of halogen ions at the anode, there occurs the irreversible formation of hydrogen peroxide as a result of the combination of discharged hydroxyl ions. The peroxide is able, under suitable conditions, to oxidize the halide ions to form free halogen or else it may decompose to yield oxygen. The accumulation of the latter determines the electrode potential, and so any factor tending to bring about decomposition of hydrogen peroxide, e.g. alkalinity, catalysts, increase of temperature, will favour the onset of the upper potential stage, when the gas evolved contains a large proportion of oxygen. Not only does the ease of halogen ion discharge increase in the order chlorine, bromine, iodine, but the rate of the oxidation of the ions to free halogen by means of hydrogen peroxide also increases in the same order: hence the accumulation of oxygen will be smallest in a solution of iodide, and the rise of potential will occur least readily under comparable conditions.

The discharge and depolarization of chlorine are important in connection with the alkali-chlorine industry.†

Valve Electrodes—In some cases the film formed on an anode is non-porous and a non-conductor; electrons cannot pass through it readily, and hydroxyl and other anions cannot be discharged at it. This behaviour is observed, for example, at an aluminium anode in a borate, phosphate or other solution. If a steadily increasing voltage is applied to a cell with an aluminium anode in a borate solution, the potential of the electrode rises rapidly at first to about 100 volts, but no appreciable current passes; the potential then increases more slowly until a value of 300–400 volts (or more) is reached when current passes as the result of a spark discharge. A film of oxide begins to form on the anode right at the commencement, but this is not quite non-porous and so allows anions to penetrate which react with the anode and cause the film to increase in thickness. The thickness increases with the applied voltage and the time of application; the value has been estimated as 109μ for aluminium at 500 volts. No appreciable current will flow even if several hundred volts are applied to such an anode,

* Glasstone and Hickling, *loc. cit.*

† See Foerster, *Elektrochemie wässriger Lösungen*, 1922, Chap. 14; Allmand and Ellingham, *Applied Electrochemistry*, 1924, Chap. XVIII; Engelhardt, *Handbuch der technischen Elektrochemie*.

but if the current is reversed, so that the aluminium becomes the cathode, appreciable currents can pass with quite small voltages. The electrode thus behaves as a valve, and permits current to flow in one direction only; * valve action has been observed with tantalum, niobium, antimony, bismuth, silver, copper, magnesium, zinc and cadmium, although with the last three metals carefully controlled conditions are necessary.† The anode voltage required to force current through the protective surface film varies with the nature of the electrode and electrolyte; thus antimony in hydrochloric acid may attain a maximum voltage of about 500 volts, but in nitric acid there is no film formation, or valve action. Silver and copper anodes attain potentials of only 50 volts in hydrobromic and hydrofluoric acids respectively; aluminium and tantalum produce films and show valve action in most electrolytes, although sulphates and particularly chlorides inhibit the film formation.‡

According to Güntherschulze, who has made many investigations in connection with valve action,§ the anode film is in two sections. The first, nearest the anode, which is about one-tenth of the whole thickness, contains oxygen gas; this is closed in by a layer containing electrolyte, but the resistance is higher than in the bulk of the solution. Current can pass only by 'gas discharge' through the gas layer, but as the electrodes are different—metal one side and oxide film on the other—the potential necessary to cause this discharge is different in the two directions. Apparently electrons pass readily from the metal to the solution at a comparatively low potential, but a much larger potential is required for passage in the opposite direction. Müller and Konopicky|| have observed that hydrogen is evolved from an aluminium valve anode; hence the latter must be in an active condition, the hydrogen resulting from local action. It has been suggested that the oxide, or hydroxide, film formed on the aluminium is a negatively charged gel; when the electrode is acting as anode the film is pressed tightly to it and so prevents dissolution and anion discharge. If the aluminium is made a cathode the film is loosened from the electrode; access of electrolyte is then possible and current can flow. At the same time spontaneous dissolution of the metal may occur, and hydrogen be evolved. A further discussion

* The valve action of Al and Ta is frequently used for rectifying A.C.

† Buff, *Annalen*, 1857, 102, 269; Norden, *Z. Elektrochem.*, 1899, 6, 159, 188; Fischer (E.), *Z. physikal. Chem.*, 1904, 48, 177; Roloff and Siede, *Z. Elektrochem.*, 1906, 12, 670.

‡ Bairsto and Mercer, *Trans. Faraday Soc.*, 1911, 7, 13.

§ For references see Müller (W. J.) and Konopicky, *Z. physikal. Chem.*, 1929, 141, 343; also *Trans. Faraday Soc.*, 1914, 9, 265.

|| *Loc. cit.*; *Z. physikal. Chem.*, 1929, 145, 241; see Evans *J. Soc. Chem. Ind.*, 1930, 49, 92 T.

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of this complicated and controversial subject is beyond the scope of this book.*

* For references to recent work, see Dobiaš *et al.*, *Z. Physik*, 1930, 61, 852; Lilienfeld *et al.*, *Trans. Amer. Electrochem. Soc.*, 1930, 58, 285; Güntherschulze, *Z. Physik*, 1931, 68, 145; *Z. Elektrochem.*, 1931, 37, 726; Newbery, *Proc. Roy. Soc.*, 1932, 137 A, 134; Müller (W. J.), *Z. Physik*, 1931, 73, 560; *Z. Elektrochem.*, 1936, 42, 166.

CHAPTER XX

ELECTROLYTIC DEPOLARIZATION

DISSOLUTION and Corrosion of Metals*—According to the views already developed any metal with an electrode potential more negative than that of hydrogen in a given electrolyte should displace this element from solution. Thus, lead (standard potential -0.12) should dissolve readily in hydrochloric acid with the evolution of hydrogen (reversible potential, approx. ± 0.0), and zinc (-0.76) should displace the latter from a neutral solution, e.g. sodium sulphate, in which the reversible hydrogen potential is about -0.41 volt. In actual practice neither of these reactions occurs, because of the hydrogen overvoltage which applies here as for evolution of the gas during ordinary electrolysis; the overvoltages of lead and zinc are 0.64 and 0.7 respectively, and hydrogen evolution can only commence at -0.64 volt in hydrochloric acid for lead, and -1.11 volt from zinc in a neutral solution. By increasing the hydrogen ion concentration the poten-

* A great deal of investigation has been carried out on this subject from the practical and theoretical standpoints; the theory of corrosion developed here is based on the views first suggested by Whitney (*J. Amer. Chem. Soc.*, 1903, 25, 394), and which have since been considerably extended. For various studies of corrosion—mainly of theoretical interest—and for full references, consult: Speller, *Causes and Prevention of Corrosion*; Evans (U. R.), *Corrosion of Metals*; Vernon, *A Bibliography of Metallic Corrosion*, 1928; Hedges, *Protective Films on Metals*; *Ann. Reports Chem. Soc.*, 1934, 31, 135; Rabald, *Werkstoffe—Physikalische Eigenschaften und Korrosion*, Vol. I; General Discussions, *Trans. Faraday Soc.*, 1915, 11; 1923, 19; Symposium, *Ind. Eng. Chem.*, 1925, 17, 335–89; Friend, *J. Chem. Soc.*, 1921, 119, 932; Evans, *J. Inst. Metals*, 1923, 30, 239; Bancroft, *J. Physical Chem.*, 1924, 28, 785; McCulloch, *Trans. Amer. Electrochem. Soc.*, 1926, 50, 379; Thiel and Eckell, *Z. Elektrochem.*, 1927, 33, 370; Pietsch and Josephy, *ibid.*, 1931, 37, 823 (summary and references); Tödt, *Z. physikal. Chem.*, 1930, 148, 434; Watts, *Trans. Amer. Electrochem. Soc.*, 1933, 64, 219; Evans and Hoar, *Trans. Faraday Soc.*, 1934, 30, 424. For dissolution of metals in acids, see Centnerszwer, *Z. physikal. Chem.*, 1929, 141, 167, 297; 1934, 167, 421; Straumanis, *ibid.*, 1930, 147, 161; 148, 349; Tammann, *Z. anorg. Chem.*, 1931, 201, 225; Müller (E.) *Z. Elektrochem.*, 1932, 38, 901; for new viewpoints, see Kilpatrick (M.) and Rushton, *J. Physical Chem.*, 1930, 34, 2180; Brønsted and Kane, *J. Amer. Chem. Soc.*, 1931, 53, 3624. For corrosion and dissolution of solid solutions, see references to Tammann and to Le Blanc, on p. 476 *supra*.

tial for gas evolution is made less negative, and so the tendency for the metal to dissolve is increased. Thus in a $2N$ -solution of strong acid the reversible hydrogen potential is about ± 0.0 , and so gas should be evolved at a zinc electrode at -0.7 volt; hence zinc would be expected to dissolve slowly in dilute acid. Actually impure zinc dissolves readily partly because its overvoltage is less than 0.7 , and partly for other reasons which will be made clear shortly; *pure* zinc, however, in agreement with theory, is only attacked slowly by dilute acids.

If the pure zinc is connected with a piece of copper and both dipped into dilute acid so as to form a short-circuited simple voltaic cell, the rate of dissolution of the zinc is markedly increased, but the hydrogen appears at the copper electrode. The less noble metal, zinc, dissolves to form zinc ions at the negative electrode, and hydrogen ions are discharged at the copper; since the overvoltage at copper is only about 0.2 volt, hydrogen evolution occurs readily and the dissolution of zinc continues. The rate at which the zinc dissolves is mainly governed by Faraday's laws; hence this is greater the higher the value of the current flowing in the short-circuited cell. Increase of current and increased rate of dissolution may be obtained by improving the conductance of the electrolyte and by raising the potential difference between the two electrodes. The latter may be achieved by making the potential of the positive electrode (e.g. copper) more positive (*a*) by increasing the hydrogen ion concentration of the solution, and (*b*) by using an electrode of lower overvoltage. In order to make the zinc dissolve rapidly it is not necessary, however, to connect it with another metal in the form of an ordinary galvanic cell; a simpler and better device is to bring the two metals in contact under the surface of the dilute acid. The same short-circuited cell is formed, but with a lower resistance, and so ready dissolution of the zinc occurs. A similar result may be obtained by adding a small quantity of copper sulphate to the solution in which the zinc is dissolving; copper is deposited, by replacement, on various parts of the zinc and a large number of local short-circuited elements are set up. In these elements the zinc is negative and dissolves, whereas the hydrogen is liberated on the copper deposit.*

Zinc may be taken as typical of a base metal with a high overvoltage and copper of a noble metal with a low overvoltage, and the results obtained are of general applicability. Whenever a metal is in contact with, has deposited on it, or included within it as a

* In a short-circuited local element, as in an ordinary voltaic cell, the portion which dissolves, that is the portion with the more negative potential, is said to be anodic, with respect to the place where hydrogen is evolved; the latter portion is termed cathodic.

separate phase, a nobler metal having a low hydrogen overvoltage, galvanic elements can be set up,* and the rate of dissolution or corrosion of the base metal is increased; this rate is greater the higher the conductance and the hydrogen ion concentration of the corroding solution, and the lower the overvoltage of the noble metal. Raising the temperature lowers overvoltage, and so, as well as for other reasons, increases corrosion. A high overvoltage metal like lead, although more noble, will not aid the dissolution of zinc at low temperature, but should do so in the vicinity of 100°.† An impure metal, e.g. zinc or iron, containing noble inclusions of low overvoltage is attacked much more readily than is the pure metal, since local elements are set up on the impure material. This mode of attack is sometimes called the 'hydrogen evolution' type of corrosion, since gas is actually evolved at the more positive portions of the metal. It is important to remember that this can only occur if the electrode potential of the base metal is more negative than that at which hydrogen evolution, allowing for overvoltage, occurs at the more positive metal or inclusion. By reducing the hydrogen ion concentration of the solution the latter potential is made more negative, and so there is frequently a pH value at which this type of corrosion ceases.

In the foregoing discussion the possibility has not been considered of using a depolarizer to prevent the accumulation of hydrogen at the more positive electrode; if this were done the potential would be made more positive and there would be an increase in the rate of dissolution of the baser metal. Unless special precautions are taken to exclude air, a depolarizer, viz. oxygen, is always present during the attack of a metal; in these circumstances the hydrogen overvoltage of the positive metal is not so important as its nobility. Thus at a local, or other element, consisting of two metals in contact with a solution in the presence of sufficient air, the less noble metal will dissolve irrespective of the hydrogen overvoltage at either metal; for this reason the iron in imperfect 'tin plate' is readily corroded in air, although in the absence of oxygen the high overvoltage at tin would prevent appreciable attack of the iron.‡

Even in the presence of a depolarizer the rate of corrosion of

* Cf. Cushman, *Trans. Amer. Electrochem. Soc.*, 1907, 12, 403.

† Centnerszwer, *Z. physikal. Chem.*, 1918, 92, 563; Evans, *J. Inst. Metals*, 1923, 30, 254.

‡ It is generally known that imperfect 'tin plate' rusts more readily than does iron alone, since, in the former case, local galvanic elements are set up in which the iron is anodic. In citric and oxalic acid solutions, however, the tin ions are removed in the form of complex anions, and the iron becomes cathodic relative to the tin (Hoar, *Trans. Faraday Soc.*, 1934, 30, 472).

the metal depends on the current flowing in the local elements; increasing the conductance of the corroding solution, and the difference of potential between positive and negative portions of the metal therefore increases the rate of attack. The positive electrodes may be regarded as a species of oxygen electrode, and so the potential is made more positive by increasing the hydrogen ion concentration of the solution; hence corrosion in the presence of a depolarizer is also favoured by increased acidity.*

Although corrosion is favoured by a large difference of potential between positive and negative portions of a metal, even the smallest of such differences is sufficient to stimulate corrosion in the presence of a depolarizer. In an apparently uniform piece of metal any portion which has been subjected to strain is generally less noble than an unstrained portion, and small crystals are less noble than large ones; † local galvanic elements of small *E.M.F.* can thus be set up, and in the presence of a depolarizer corrosion of the baser portions of the metal will occur. ‡ That a comparatively uniform piece of iron has positive and negative portions has been shown by a striking experiment devised by W. H. Walker, Cederholm and Bent, § and modified by Cushman and Gardner. || A little potassium ferricyanide and some phenol phthalein are added to a solution of sodium chloride, or other suitable corroding medium; sufficient agar is then added for a jelly to form in the cold. The resulting mixture is called the 'ferroxyl' indicator. The warm solution is poured on to a uniform piece of iron, allowed to set and put aside for a short time; since ferrous ions are formed at the negative portions of the metal—by the dissolution of the base metal, iron—they will react with the ferricyanide and produce a blue coloration. At the positive parts hydrogen ions are discharged—subsequently oxidized by the ferricyanide—and so the solution there becomes alkaline and the phenol phthalein is turned pink. The positive and negative portions of the iron can thus be clearly distinguished.**

Since corrosion is generally attributed to galvanic action it has frequently been considered that a perfectly homogeneous metal

* Iron corrodes more readily in very concentrated alkali than in solutions of lower pH. The ferrous 'hydroxide' films formed over the negative portions in feebly alkaline solution preserve the metal from attack, but they dissolve in concentrated alkali and corrosion increases.

† Cf. Walker (W. H.) and Dill, *Trans. Amer. Electrochem. Soc.*, 1907, 11, 153; Burgess, *ibid.*, 1908, 13, 17.

‡ Rawdon, *Ind. Eng. Chem.*, 1927, 19, 613.

§ *J. Amer. Chem. Soc.*, 1907, 29, 1256.

|| *Corrosion and Preservation of Iron and Steel*, 1910, p. 48.

** For applications, see Cobb, *J. Iron and Steel Inst.*, 1911, 83, 170; Evans, *J. Oil Col. Chem. Assoc.*, 1923, 6, 155; *Metal Ind. (London)*, 1926, 29, 481, 507.

would not be attacked, even in the presence of a depolarizer.* It is doubtful, however, if this concept, even if correct, is of any value, since it seems impossible to obtain absolute uniformity; even in a large single crystal of a metal it is not improbable that the 'solution pressure' would be different at different faces, and hence corrosion would occur. Further, the uniformity would have to extend to the solution in which the metal was placed, otherwise local elements could exist.

Hitherto it has been assumed that the corroded metal is a base one, and has a more negative potential than hydrogen, but the conclusions regarding corrosion in the presence of a depolarizer are applicable to all metals. Thus, copper is normally insoluble in cold dilute sulphuric acid, but it will dissolve if air is bubbled through the solution, or if hydrogen peroxide is added.† Copper cannot cause the evolution of hydrogen from sulphuric acid,‡ but if it is brought into contact with a more noble metal a galvanic element will be set up, and copper will dissolve to a minute extent; hydrogen ions will be discharged at the nobler (more positive) metal until the potential is the same as that of the copper, then all action ceases. As the potential of copper is generally positive with respect to that of hydrogen, only a very minute accumulation of the latter is necessary for this condition to be reached, and the copper remains almost unattacked. If, however, a depolarizer is present the discharged hydrogen is oxidized and removed as fast as it is formed, and dissolution of the copper continues. In general a second, more noble, metal is not necessary to aid the dissolution of copper, since irregularities in the metal itself are sufficient to set up galvanic elements. Nitric acid is a good depolarizer, and so copper dissolves readily in it, but hydrogen cannot, of course, be evolved; the substances obtained are reduction products of the nitric acid.

An important type of corrosion which has been studied in recent years § results when the distribution of depolarizer, generally

* Lambert, *J. Chem. Soc.*, 1912, 101, 2056; 1915, 107, 218; Bengough and Stuart, *J. Inst. Metals*, 1922, 28, 54; Palmaer, *Korr. und Metallschutz*, 1926, 2, 3.

† See Watts and Whipple, *Trans. Amer. Electrochem. Soc.*, 1917, 32, 257.

‡ Copper liberates hydrogen gas from hydrobromic acid and from potassium cyanide solution, since complex ions are formed.

§ Aston, *Trans. Amer. Electrochem. Soc.*, 1916, 29, 449; Evans, *J. Inst. Metals*, 1923, 30, 61; *J. Soc. Chem. Ind.*, 1924, 43, 129 T, 315 T; 1926, 45, 38 T; *Ind. Eng. Chem.*, 1925, 17, 363; *J. Chem. Soc.*, 1929, 92. For discussions of the subject, see Bengough *et al.*, *Proc. Roy. Soc.*, 1927, 116 A, 451; 1928, 121 A, 88; 1930, 127 A, 42; 1931, 131 A, 494; 134 A, 308; 1933, 140 A, 399; Liebreich, *Z. physikal. Chem.*, 1931, 155, 123; 1932, 160, 211; Schickorr, *ibid.*, p. 205; Evans *et al.*, *ibid.*, p. 194; *Proc. Roy. Soc.*, 1932, 137 A, 343; 1934, 146 A, 153; Hoar, *ibid.*, 1933, 142 A, 628.

oxygen, is not uniform over the surface of the metal; this has been called corrosion due to 'differential oxygenation'. If oxygen has access to certain portions of a metal, depolarization of hydrogen will occur more readily there, and the potential will be more positive than on the other parts; the latter portions will, therefore, tend to dissolve because an *E.M.F.* is produced. It seems anomalous, at first sight, that the parts of the metal to which the oxygen has *not* access dissolve, whereas the oxygenated portions do not dissolve; this is because depolarization occurs at the latter parts, and hydrogen ions will be discharged there to replace the atoms removed by oxidation. This mechanism accounts for the fact that rusting of iron occurs preferentially under portions covered with wet rust. Air has not access to these parts; hence they become negative in potential, that is anodic, with respect to the others, and continue to dissolve as long as depolarization proceeds. The same argument holds for the corrosion of any metal covered with a *partially* protective film. Corrosion at the bottom of 'pits' in a metal surface is due to the same cause. The formation of oxide films, tending to encourage passivity, also helps those parts of the metal exposed to oxygen to become cathodic, thus favouring the attack on the other portions.

Rusting of Iron*—In the course of much investigation of this subject it became clear that rusting is favoured by (a) impurities in the metal; (b) contact with more noble metals; (c) the presence of moisture; (d) the presence of carbon dioxide; and (e) oxygen. The first two factors facilitate the production of galvanic elements, whereas the third is essential, as it provides a medium for the flow of current; the presence of electrolytes also helps in this respect. Carbon dioxide decreases the *pH* of the corroding solution, and hence increases the *E.M.F.* of local elements, but its presence is not essential to corrosion. Oxygen acts as a depolarizer; when it has uniform access it accelerates corrosion of the baser portions—generally iron—but when its access is non-uniform the less oxygenated parts are preferentially corroded. In the absence of oxygen very little corrosion of iron would occur unless the *pH* of the solution were fairly low, and the noble impurities had a low overvoltage.† When the alkali formed at the positive portions of the iron meets the solution of ferrous salt formed by the dissolving negative portions, ferrous hydroxide is precipi-

* For full account and references see Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. XIII, 1934, p. 403.

† With pure iron, chromium and certain alloys, e.g. stainless steel, uniform access of oxygen results in the formation of an oxide film which renders the metal passive and immune from further attack. Chlorine ions, however, appear to be able to penetrate such films and in their presence corrosion will occur.

tated; this is subsequently oxidized to the ferric state and forms the basis of rust. It is important to remember that in the rusting of iron, as in other cases, several types of corrosion may be occurring simultaneously.

Depolarization in Primary Cells—Just as the presence of a depolarizer in the vicinity of the cathodic portion of a short-circuited local element favours corrosion, so a substance able to react with hydrogen will prevent polarization in a galvanic cell which is being used as a source of current. The earliest primary cells, consisting of two metals, e.g. zinc and copper, dipping in an acid solution were unsatisfactory since the *E.M.F.* rapidly decreased from its initial value owing to the polarization set up by the hydrogen at the cathode: the presence of a suitable oxidizing agent to act as depolarizer, however, prevents the liberation of hydrogen and a relatively constant *E.M.F.* can be obtained. The actual voltage of the cell depends partly on the nature of the anodic metal, generally zinc, and partly on the oxidation potential, not always reversible, however, of the depolarizer. Various materials have been suggested for the latter, the best known being nitric acid in the Grove cell, chromic acid in the Poggendorff cell, manganese dioxide in the Leclanché cell, cupric oxide in the Lalande cell, and air in the Fery cell.*

Electrolytic Reduction and Oxidation—Oxidation and reduction may be regarded as the removal and addition of electrons respectively; when a current from an external battery is applied to a pair of electrodes so as to make them anode and cathode respectively, the former can act as a continuous remover of electrons and the latter as a continuous source of supply. It appears, therefore, that in general electrolytic oxidation may be brought about at an anode and reduction at a cathode. Oxidation and reduction reactions may be classified as reversible and irreversible, and these types will be considered separately.

Reversible Oxidation-Reduction Reactions†—The principle involved is identical with that applicable to the reversible deposition or dissolution of metals. If the potential of a cathode

* For full descriptions and references, see Foerster, *Elektrochemie wässeriger Lösungen*, 1922, p. 237; Allmand and Ellingham, *Applied Electrochemistry*, 1925, p. 207; Güntherschulze, *Galvanische Elemente*, 1928; Walden-Drucker, *Handbuch der Allgemeinen Chemie*, 1930, Vol. VIII, Part I, p. 744 (Kremann and R. Müller). For recent studies, see Gruhl, *Z. Elektrochem.*, 1925, 31, 214; Keller, *ibid.*, 1931, 37, 342; Thielmann, *ibid.*, 1933, 39, 782; Drucker, *Z. physikal. Chem.*, 1931, Bodenstein Festband, 912 (Leclanché type of cell); Tobler, *Z. Elektrochem.*, 1933, 39, 148; Baur, *ibid.*, 1934, 40, 249 (air cell).

† For numerous examples with references, see Glasstone and Hickling, *Electrolytic Oxidation and Reduction*, 1935.

is made just more negative than the reversible oxidation-reduction potential of the solution in which it is placed, reduction will commence; when the anodic potential exceeds the reversible value, oxidation results. Thus if two platinum electrodes are placed in an acid solution containing equi-molar amounts of ferrous and ferric salts ($\pi = 0.74$), and a gradually increasing *E.M.F.* applied, oxidation of ferrous to ferric ions will commence at the anode when its potential is just greater than $+0.74$ volt; reduction to ferrous ions at the cathode will occur when its potential is slightly more *negative* than $+0.74$ volt.* As the current is increased the rapid rate of oxidation or reduction will bring about concentration changes in the vicinity of the electrodes which cannot be rectified by diffusion from the bulk of the solution; a type of concentration polarization then results. The anode potential becomes somewhat more positive, since the ratio of $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ is greater than at the commencement, and the cathode potential becomes more negative; these changes are most marked if the solution is dilute, but they can be reduced if the solution is stirred or the temperature raised.† If the *C.D.* is very high the rate of oxidation or reduction may exceed the rate of diffusion of ions to the anode or cathode, and another *simultaneous* process must occur in order to maintain the current. This may be at the anode (a) another oxidation reaction; (b) discharge of chlorine ions and evolution of chlorine gas, if the solution contains chlorides; ‡ (c) evolution of oxygen; and (d) dissolution of the anode itself. Such additional processes are invariably accompanied by an increase of potential, each occurring as the appropriate potential is attained. The maximum *C.D.* attainable before the alternative process commences is generally called the limiting current density: its value depends on the conditions of electrolysis and the concentration of the solution. The behaviour of the cathode is similar; the primary reduction process may be accompanied at high *C.D.*'s by (a) another reduction; (b) deposition of a metal; or (c) liberation of hydrogen.§

In some cases the oxidation-reduction potential may have such a value that another process occurs simultaneously. Thus the reversible potential in an acid solution of equi-molar amounts of titanous and titanous ions is about $+0.05$ volt, and when using a platinized platinum cathode hydrogen evolution commences as soon as the potential is about ± 0.0 volt; the reduction cannot, therefore, be carried out very rapidly. With a smooth platinum elec-

* The potentials should be independent of the electrode material.

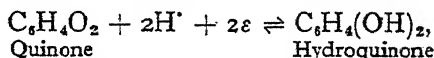
† Cf. Karaoglanoff, *Z. Elektrochem.*, 1906, 12, 5; Wilson and Youtz, *Ind. Eng. Chem.*, 1923, 15, 603; Moll, *Z. physikal. Chem.*, 1936, 175, 353.

‡ See Wilson and Youtz, *loc. cit.*

§ Oettel, *Z. Elektrochem.*, 1894, 1, 91.

trode, however, the overvoltage is greater and hydrogen evolution is delayed until a potential of about -0.1 volt.* In the cathodic reduction of stannic to stannous ions in hydrochloric acid solution, simultaneous deposition of tin and liberation of hydrogen occur, especially at low temperatures.† It has been assumed hitherto that reversible oxidation or reduction processes involving ions are not accompanied by any appreciable polarization apart from that due to concentration changes: this is, however, not always the case. The reductions of V^V to V^{IV} and of V^{IV} to V^{III} ,‡ of Mo^V to Mo^V and of Mo^V to Mo^{III} ,§ and of W^VI to W^V || are all accompanied by marked polarization at smooth platinum cathodes, although it is less with platinized platinum electrodes. The abnormal behaviour in all these substances is probably to be attributed to the presence of oxides on the cathode: these have the effect of blocking most of the surface so that the effective *C.D.* is very high. The oxidation of chromic ions to chromate shows unusual phenomena,** but the process is probably not reversible: considerable polarization accompanies the reverse reaction and oxides are formed on the cathode.††

The oxidation-reduction system of quinone and hydroquinone, i.e.



is undoubtedly reversible, and definite static potentials, varying in the expected manner with the hydrogen ion concentration (see p. 378) are obtained at various unattackable electrodes, e.g. platinum, smooth and platinized, copper, silver and mercury. If an acid solution of quinhydrone, that is one containing equimolecular amounts of quinone and hydroquinone, is oxidized or reduced at a platinized platinum anode or cathode, respectively, the polarization observed is small (Fig. 38, curves A_2 and C_2); it is, in fact, not more than might be expected from concentration polarization with any reversible process. At smooth platinum, copper, silver or mercury electrodes, however, there is considerable polarization (curves A_1 and C_1), although the correct *static* potentials are indicated by these materials.‡‡ This result was explained by supposing that, although the oxidation and reduction processes are reversible, they are fundamentally slow reactions,§§ which can presumably be

* Diethelm and Foerster, *Z. physikal. Chem.*, 1908, **62**, 129.

† Foerster and Yamasaki, *Z. Elektrochem.*, 1911, **17**, 366.

‡ Foerster and Böttcher, *Z. physikal. Chem.*, 1930, **151**, 321.

§ Foerster *et al.*, *ibid.*, 1930, **146**, 81, 177.

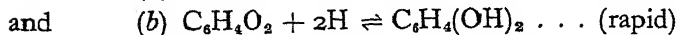
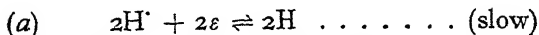
|| Glasstone and Hickling, *op. cit.*, p. 135. ** *Idem.*, *op. cit.*, p. 123.

†† Cf. Müller (E.), *Z. Elektrochem.*, 1899, **5**, 469; 1901, **7**, 398.

‡‡ Russ, *Z. physikal. Chem.*, 1903, **44**, 641.

§§ Haber and Russ, *ibid.*, 1904, **47**, 257.

catalysed by the electrode material. Measurements of the limiting *C.D.* for the oxidation of hydroquinone or the reduction of quinone suggest, however, that the chemical parts of reactions are probably rapid,* and the slowness is to be found in the ionization stages : thus



This suggestion brings the observations into line with the modern theory of hydrogen overvoltage (p. 442) which suggests a slowness in the neutralization of hydrogen ions, and presumably in the ionization of the atoms : the process should, however, be rapid at platinized platinum, since it has a low overvoltage.

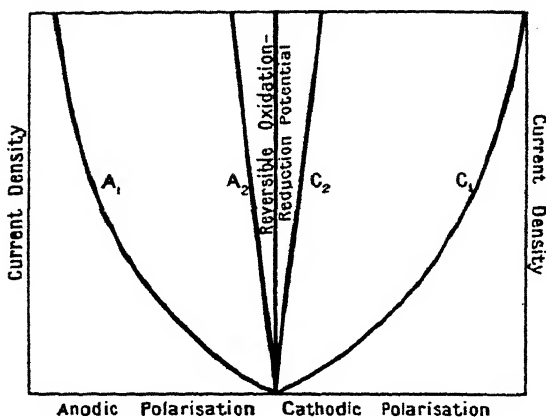


FIG. 38.—Polarization-current density curves for a reversible oxidation-reduction system

Polymerization of Anions—The type of anodic oxidation, of which the formation of persulphuric acid is one of the best-known instances, involving the union of two or more anion residues was at one time thought to be reversible : it is very doubtful, however, whether any of the known cases can be regarded as being reversible in the thermodynamic sense. It is, nevertheless, convenient to consider these reactions separately from completely non-reversible processes. The anodic formation of persulphuric acid by the electrolysis of sulphuric acid was known to Berthelot,† but solid persulphates were first obtained in an analogous manner by Marshall.‡ The production of the free acid is favoured by high sulphuric acid concentration and by high *C.D.*, although there are optimum values

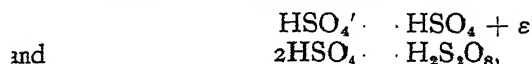
* Glasstone, unpublished data.

† *Compt. rend.*, 1878, 86, 20, 71, 277, etc.

‡ *J. Chem. Soc.*, 1891, 59, 771; *J. Soc. Chem. Ind.*, 1897, 16, 396.

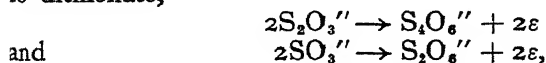
for both these quantities : * this limit may be connected with the tendency for persulphuric acid ($\text{H}_2\text{S}_2\text{O}_8$) to hydrolyse in acid solution to yield Caro's acid (H_2SO_5), the latter itself being a depolarizer and so uses up some of the current.† Solutions of alkali or ammonium sulphates form persulphates at the anode, the efficiency decreasing in the order ammonium, potassium, sodium.‡ The best results are obtained with a smooth platinum anode, and the addition of fluoride to the electrolyte increases the yield of persulphate.§

It was originally assumed that the formation of persulphate was to be attributed to the polymerization of HSO_4 radicals formed by the discharge of bisulphate ions, thus



but this view is not now universally accepted. It is true that there is a parallelism between the HSO_4' concentration in sulphuric acid solutions and the yield of persulphuric acid,|| but the theory does not account for the fact that the efficiency is greater in a solution containing ammonium sulphate only than in one with an equivalent amount of acid only. There is a possibility that persulphates may result from chemical oxidation by means of oxygen, or other active agent, formed at the anode,** and it is significant that appreciable amounts of persulphate result from the action of fluorine gas on bisulphate solutions.††

The oxidation of thiosulphate to tetrathionate and of sulphite to dithionate,



may be formulated as electrical processes involving the discharge of $\text{S}_2\text{O}_3''$ or SO_3'' ions, but there is a decided opinion in favour of a purely chemical mechanism for these reactions. Glasstone and Hickling ‡‡ have made a comprehensive study of these anodic processes and have observed two potential stages at a platinum anode,

* Elbs and Schönherr, *Z. Elektrochem.*, 1894, 1, 417.

† Müller (E.) and Schellhaas, *ibid.*, 1907, 13, 257.

‡ Cf. Elbs and Schönherr, *ibid.*, 1895, 2, 245; Essin and Alfimova, *ibid.*, 1935, 41, 260; and unpublished observations.

§ Müller (E.), *ibid.*, 1904, 10, 776.

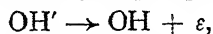
|| Starck, *Z. physikal. Chem.*, 1899, 29, 385.

** Foerster, *Elektrochemie wässriger Lösungen*, 1922, p. 842; Essin, *Z. physikal. Chem.*, 1933, 164, 87; *Z. Elektrochem.*, 1933, 39, 891.

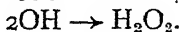
†† See, for example, Fichter and Humpert, *Helv. Chim. Acta*, 1923, 6, 640.

‡‡ *J. Chem. Soc.*, 1932, 2345, 2800; 1933, 829; references to previous work are given in full.

but the oxidation efficiency is almost the same at both stages. Catalysts for hydrogen peroxide decomposition cause the electrode potential to rise rapidly, but they inhibit the formation of tetrathionate and dithionate from thiosulphate and sulphite respectively. To account for these and many other observations it is suggested that when hydroxyl ions are discharged at an anode the radicals combine *irreversibly* to form hydrogen peroxide, thus



followed by



Since the latter process is irreversible the discharge of hydroxyl ions and formation of peroxide should be able to take place at potentials much below the normal discharge potential. It is supposed that the hydrogen peroxide can then either react with the thiosulphate or sulphite, or else decompose to yield oxygen: any factor, e.g. catalysts, favouring the latter alternative will result in an increase of anode potential and a decrease of efficiency. With certain catalysts for decomposition of hydrogen peroxide, e.g. manganese salts, there is a tendency for the dioxide to deposit on the anode, and it has been suggested that the anode oxidation, e.g. of sulphite, is really a purely electrochemical one involving discharge of $\text{SO}_3^{\cdot\cdot}$ ions, but the process cannot occur at the dioxide electrode,* or that the lower overvoltage at the latter than at the clean platinum results in a decrease of efficiency † (cf. p. 521). It has been pointed out, however, ‡ that there is no parallelism between anodic overvoltage and the efficiency of various processes involving the polymerization of anions; further, there appears to be no simple reason for supposing that $\text{SO}_3^{\cdot\cdot}$ ions will discharge at a platinum anode but not at one covered with a dioxide, in spite of the higher potential of the latter. It is doubtful whether any theory hitherto proposed is able to account for so many of the observations made on the oxidation of thiosulphate and sulphite ions as that based on the irreversible formation of hydrogen peroxide.

Other examples of the electrolytic polymerization of anions are the conversion of carbonate to percarbonate and of phosphate to perphosphate: a comprehensive investigation of the latter process has been made by Partington and Husain.§ There is strong evidence in favour of the view that these reactions are brought about by a chemical oxidizing agent which is produced by the current, and not by the direct discharge of the carbonate or phosphate ions.||

* Butler and Leslie, *Trans. Faraday Soc.*, 1936, **32**, 435.

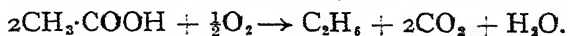
† Walker (O.J.) and Weiss, *ibid.*, 1935, **31**, 1011.

‡ Glasstone and Hickling, *ibid.*, p. 1656.

§ *Trans. Faraday Soc.*, 1928, **24**, 235.

|| For further references and discussion of these and other processes see Glasstone and Hickling, *op. cit.*, Chap. VII.

Oxidation of Fatty Acids and Salts—The phenomena observed in the electrolysis of acetates have a number of features in common with those found in the reactions just discussed and so the subject will be considered next. Whilst attempting to isolate the methyl radical, Kolbe* electrolysed an aqueous solution of potassium acetate, and obtained at a smooth platinum anode a mixture of ethane and carbon dioxide; the net reaction is evidently



The Kolbe electrolytic oxidation appears to be quite general for most salts of aliphatic, but not aromatic, acids, as well as for the free acids themselves, and by its use paraffin hydrocarbons up to $\text{C}_{34}\text{H}_{70}$ have been obtained.† Increase of temperature decreases the efficiency of the Kolbe reaction in aqueous solutions, and only relatively small amounts of hydrocarbon are obtained at platinized platinum, palladium, gold, nickel and iron anodes. If platinized platinum is previously polarized anodically, however, or poisoned with mercury, the Kolbe synthesis takes place to an appreciable extent.‡ The presence of catalysts for hydrogen peroxide decomposition, either those which give peroxide deposits on the anode, e.g. manganese and lead salts, or those which do not, e.g. iron salts, brings about a decrease in the formation of ethane when an aqueous solution of acetate is electrolysed.§ If salts are added to the electrolyte, especially if this consists of acetic acid only, the extent of the Kolbe reaction is also diminished.|| In both these cases a large proportion of the current oxidizes the acetate, or acetic acid, to methyl alcohol: this is known as the Hofer-Moest reaction. At low *C.D.*'s, or when the Kolbe reaction is suppressed by either of the methods just described, the gas evolved at the anode contains appreciable amounts of methane.** At a smooth platinum anode it appears that a potential of 2.15 volts must be attained before the formation of ethane occurs in an acetate solution: †† it should be noted that this potential is greater than that at which oxygen evolution should occur in the solutions used, although only

* *Annalen*, 1849, 69, 279.

† Petersen, *Z. Elektrochem.*, 1906, 12, 142.

‡ Foerster and Piguet, *Z. Elektrochem.*, 1904, 10, 729; Preuner and Ludlam, *Z. physikal. Chem.*, 1907, 59, 670, 682; Fairweather and Walker (O. J.), *J. Chem. Soc.*, 1926, 3111; Glasstone and Hickling, *ibid.*, 1934, 1878.

§ Glasstone and Hickling, *loc. cit.*

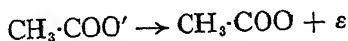
|| Hofer and Moest, *Annalen*, 1902, 323, 284; *Z. Elektrochem.*, 1904, 10, 833; see also, Matsui and Kizaki, *Mem. Coll. Sci. Kyoto*, 1933, 16 A, 297.

** Shukla and Walker (O. J.), *Trans. Faraday Soc.*, 1931, 27, 35; Glasstone and Hickling, *loc. cit.*

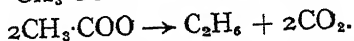
†† Shukla and Walker, *ibid.*, p. 722.

a negligible amount of this gas is actually obtained. In non-aqueous solutions the Kolbe reaction takes place with good efficiency at platinized platinum and gold, as well as at smooth platinum, electrodes; increase of temperature and the presence of catalysts for hydrogen peroxide decomposition have relatively little effect.* The anode potential at which the formation of ethane occurs appears to be about 2.15 volts with smooth and platinized platinum, gold, graphite and manganese dioxide electrodes in an ethylene glycol solution of acetate.† The mechanism of the Kolbe reaction is apparently different in aqueous and non-aqueous solutions.

In order to account for the formation of ethane, Kolbe suggested that the acetate was oxidized by anodic oxygen, but subsequently Crum Brown and J. Walker ‡ suggested that acetate ions were discharged directly at the anode and the resulting radicals then reacted, thus



and



The main evidence for this theory is that evolution of ethane does not commence until a definite anode potential is attained, but it does not readily account for the effect of different electrode materials in aqueous solutions, nor is it easy to see why there is usually little oxygen evolution in spite of the high potential. The suppression of the Kolbe synthesis by the Hofer-Moest reaction under certain conditions provides a further difficulty. Fichter § has revived in a modified form a theory originally proposed by Schall: || it is suggested that active anodic oxygen oxidizes the acetate ions or acetic acid to acetyl peroxide, $(\text{CH}_3\cdot\text{COO})_2$, which then decomposes spontaneously to yield ethane and carbon dioxide. The products of thermal decomposition of acetyl and other peroxides prepared chemically provide evidence for the theory,** but the effect of anode material, of added salts, and of catalysts for hydrogen peroxide decomposition cannot be readily explained. A point of view has been suggested by Glasstone and Hickling †† which appears to bring both theories already described into line with the suggestion that hydrogen peroxide is formed at an anode in aqueous solution by the irreversible union of hydroxyl radicals. Under normal conditions the hydrogen peroxide reacts with acetate ions to form

* For references, see Glasstone and Hickling, *J. Chem. Soc.*, 1936, 820.

† Glasstone and Hickling, *loc. cit.*

‡ *Annalen*, 1891, 261, 107; see also, Shukla and Walker, *loc. cit.*

§ Fichter and Krummenacher, *Helv. Chim. Acta*, 1918, 1, 146.

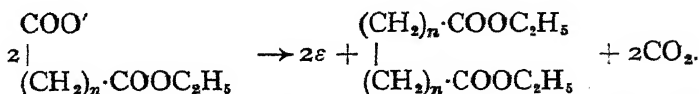
|| *Z. Elektrochem.*, 1896, 3, 86.

** For summaries, see Fichter, *Trans. Amer. Electrochem. Soc.*, 1924, 45, 131; 1929, 56, 467; *J. Soc. Chem. Ind.*, 1929, 48, 347 T, 354 T

†† *Loc. cit.*

acetate radicals, which then combine, possibly with the intermediate formation of acetyl peroxide, to yield ethane and carbon dioxide. A small proportion of the current is devoted to the direct discharge of acetate ions, followed by the reaction just mentioned. In the presence of catalysts for hydrogen peroxide decomposition, or of anions which prevent access of acetate ions to the anode, peracetic acid is probably formed by chemical oxidation and this decomposes to give methyl alcohol; the effect of anode materials can be explained in an analogous manner, by their influence on the decomposition of hydrogen peroxide. It may be noted that both ethane and methyl alcohol are obtainable under appropriate conditions by the chemical oxidation of acetate solutions by means of persulphate or fluorine.* In non-aqueous solutions hydrogen peroxide cannot generally be formed, since no hydroxyl ions are present, and hence direct discharge of acetate ions takes place at almost any anode: the radicals probably combine to form acetyl peroxide which then decomposes to form ethane. Lead monoxide is able to catalyse an alternative decomposition of this peroxide yielding oxygen, and it is important to note that the efficiency of the Kolbe synthesis in ethylene glycol is very low at an anode on which lead monoxide is formed by the reduction of the dioxide.

The salts of normal dicarboxylic acids do not undergo oxidation similar to the Kolbe synthesis, but alkali salts of the half-esterified acids do, however, give a reaction of this type; this synthesis is generally known by the names of its discoverers, Crum Brown and J. Walker.† The anodic reaction may be written in the general form



The resulting product is the ester of a dibasic acid with double the number of CH_2 groups in the original acid; the method has been used to prepare dibasic acids containing up to 32 CH_2 groups.‡ The best conditions for the Brown-Walker synthesis are similar to those applicable for the Kolbe reaction, and it is probable that the fundamental mechanisms are the same.§

Non-Reversible Oxidation and Reduction Processes—

Reactions of this type occur most frequently with un-ionized substances, e.g. organic compounds; the reduction of nitro-benzene

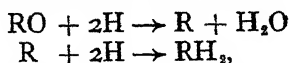
* Gordon, *J. Physical Chem.*, 1914, 18, 55; Fichter *et al.*, *Helv. Chim. Acta*, 1926, 9, 692; 1929, 12, 573, 993; 1932, 15, 996; 1933, 16, 338; Glasstone and Hickling, *loc. cit.*

† *Loc. cit.*; *Annalen*, 1893, 274, 41.

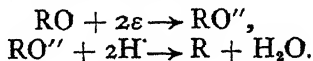
‡ Fairweather, *Proc. Roy. Soc. Edin.*, 1925, 45, 283; 1926, 46, 71.

§ Cf. Robertson, *J. Chem. Soc.*, 1925, 127, 2057.

to aniline, and oxidation of an alcohol to a carboxylic acid are examples of reactions which may be carried out electrolytically. A number of inorganic reactions, e.g. reduction of nitric acid and nitrates to hydroxylamine and ammonia, are also probably non-reversible. Although the electrolytic oxidation and reduction of organic compounds has been the subject of much study, the exact mechanism of the reactions involved is still unknown.* Reduction processes are perhaps better understood as fewer by-products are involved; cathode reactions will, therefore, be considered first. In general a non-reversible reduction may be regarded as a reaction between the reducible substance and atomic hydrogen, thus:



but it is possible that in some cases direct transfer of electrons from the cathode may be the primary process,† thus:



followed by

The velocity of the reduction process will depend, amongst other factors, on the concentrations of the reducible substance and of atomic hydrogen, and the latter will depend on the cathode potential; these variables will also determine the possibility of forming intermediate products of reduction, e.g. ROH and RH. The following factors are able to affect the course and speed of electrochemical reduction: (a) electrode potential; (b) nature and condition of the cathode; (c) concentration of the reducible compound (depolarizer); (d) temperature of the electrode and the electrolyte; and (e) the presence of catalysts; these will be discussed in turn. Since non-reversible oxidations and reductions generally involve non-ionizable substances an electrolyte must be present to conduct the current; this sometimes also has an influence on the course of the reaction.

Electrode Potential—The work of Haber ‡ has shown that by varying the electrode potential it is possible to obtain different reduction products with the same electrode; the lower the potential the smaller the concentration of active hydrogen and the less efficient the reduction process. In the absence of a depolarizer

* For full account and references, see Brockman, *Electro-Organic Chemistry*, 1926; *Bibliography of Electro-Organic Chemistry*, National Research Council, U.S.A., 1926; Foerster, *Elektrochemie wässriger Lösungen*, 1923; Glasstone and Hickling, *Electrolytic Oxidation and Reduction*, 1935.

† See Leslie and Butler, *Trans. Faraday Soc.*, 1936, 32, 989.

‡ *Z. Elektrochem.*, 1898, 4, 506; *Z. physikal. Chem.*, 1900, 32, 271; see also, Elbs, *Z. Elektrochem.*, 1900, 7, 133; Löb, *Z. physikal. Chem.*, 1904, 47, 418.

the *C.D.*-potential curve of a cathode will be of the type of Fig. 39A, but in the presence of a reducible substance the accumulation of hydrogen in some form, which is responsible for the rapid rise of potential from *a* to *b*, will not occur to such a marked extent. The electrode potential will only rise slowly with increasing *C.D.* (Fig. 39B)—the more rapid the reduction process the slower the rise—although eventually when the point *b'* is reached, approximately the same potential as *b*, gas evolution commences and the potential changes very little more. Between *a* and *b'*, however, it is possible by regulating the *C.D.* to maintain a fairly definite cathode poten-

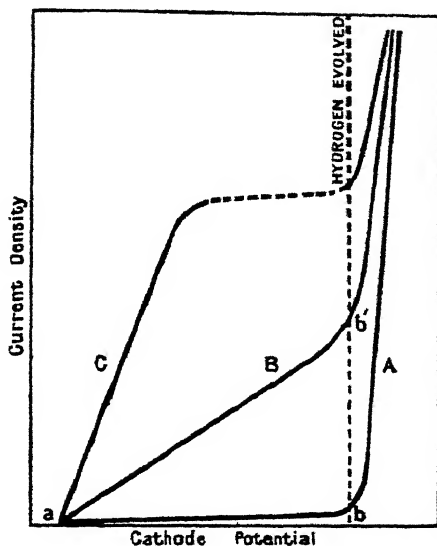


FIG. 39.—Cathode potential-current density curve for electrolytic reduction

tial; thus Haber found that with a platinum cathode in an alkaline alcoholic solution of nitrobenzene a *C.D.* of 0.001 amp. per sq. cm. gave a potential of -0.6 volt, and the chief product of electrolytic reduction was azoxybenzene. If the *C.D.* was increased to 0.0035 amp. per sq. cm. the cathode potential increased to -1.0 volt, when hydrazobenzene was produced and hydrogen evolved.

Nature of Electrode—No matter what is the actual cause of overvoltage, it is evident that since a higher potential is attainable, the higher the overvoltage of the cathode the greater should be the speed and efficiency of the reductions which can occur at such an electrode.* Further, it is probable that at the same time the

* Cf. Russ, *ibid.*, 1903, 44, 641; Haber and Russ, *ibid.*, 1904, 47, 257; see also, Kobosev and Nekrassov, *Z. Elektrochem.*, 1930, 36, 529.

most highly reduced compounds will result. With cathodes of low overvoltage, however, the reducing power, in the absence of a special catalyst, will be very small. The hydrogen evolved from such electrodes should have little more activity than the ordinary gas at atmospheric pressure. These conclusions are in agreement with the experimental results; * thus Tafel found that carbonyl compounds and pyridine and its derivatives are often difficult to reduce electrolytically, but the use of cathodes of mercury, lead or zinc enabled the reduction to occur readily. If, however, the electrodes contained impurities of low overvoltage, or if the electrolyte contained traces of salts of low overvoltage metals, e.g. copper, silver and platinum, which might be deposited on the cathode, the electrolytic reduction would be entirely inhibited. In the reduction of nitro-compounds the use of zinc, lead, tin or mercury cathodes generally results in a good yield of amine; at cathodes of nickel, carbon or platinum, however, intermediate products are obtained, e.g. phenyl hydroxylamine and benzidine from nitrobenzene.†

Although the overvoltage of the cathode metal is important in controlling the electrolytic reduction it is not always the deciding factor. For example, nitrobenzene in alkaline solution may be reduced to azoxybenzene at a platinum, nickel or mercury cathode; at a cathode of zinc, tin or lead reduction may go a stage further to hydrazobenzene.‡ Apart from the abnormal position of mercury the results are in accord with those expected from the respective overvoltages; at a copper cathode, however, in spite of the low overvoltage, reduction of nitrobenzene to aniline occurs. It is fairly certain that the copper is itself acting as a catalyst in the reduction process; in agreement with this view, the reduction efficiency at a copper cathode in acid solution is also very marked. Another instance of the catalytic influence of the cathode material, apart from its overvoltage, is found in the reduction of nitric acid in sulphuric acid solution.§ The chief products are ammonia and hydroxylamine, in the form of salts; the current efficiencies for these two substances at various electrodes are given in Table LXVII.

* Tafel *et al.*, *Z. physikal. Chem.*, 1900, 34, 187; 1905, 52, 349; Escherich and Moest, *Z. Elektrochem.*, 1902, 8, 849; Zerbes, *ibid.*, 1912, 18, 619; Shima, *Mem. Coll. Sci. Kyoto*, 1929, 12 A, 73; Sakauri, *ibid.*, 1930, 13 A, 315; for full references, see Glasstone and Hickling, *op. cit.*, Chap. V.

† Elbs *et al.*, *Z. Elektrochem.*, 1896, 2, 472; 1901, 7, 589; see also, Löb, *ibid.*, 1903, 9, 753.

‡ *Idem.*, *ibid.*, 1901, 7, 338, 597; 1902, 8, 778; *Z. physikal. Chem.*, 1904, 47, 418.

§ Tafel, *Z. anorg. Chem.*, 1902, 31, 289.

TABLE LXVII

REDUCTION OF NITRIC ACID AT VARIOUS CATHODES

Cathode Material.	Proportion of Total Current used in the Production of	
	Hydroxylamine.	Ammonia.
Lead (amalgamated)	70%	17%
Lead (roughened)	24%	61%
Zinc (smooth)	43%	
Copper (smooth)	11%	
Copper (spongy)	15%	93%

The spongy copper electrode has the lowest overvoltage, yet it is the most efficient for the reduction process; the amalgamated lead has the highest overvoltage, but appears to be least efficient. The copper evidently has a catalytic effect in the electrolytic reduction of nitric acid.

Concentration of Depolarizer—Although the concentration may not affect the nature of the reduction process it will influence the efficiency. By increasing the concentration of depolarizer the reduction velocity is increased and the slope of the cathode potential-*C.D.* curve (Fig. 39) indicates that the attainment of the potential required for hydrogen evolution is delayed. It is thus possible to get 100 per cent. reduction efficiency at high *C.D.*'s. The use of a concentrated solution, or of vigorous stirring, or both, is desirable in order to obtain the maximum yield of reduction product in a given time. If the rate of reduction is very considerable it may, at a high *C.D.*, exceed the rate at which fresh depolarizer diffuses up to the cathode; at this point another process must occur at the cathode, viz. evolution of hydrogen, and this is generally accompanied by a rapid increase of potential (Fig. 39c). Increase of concentration or stirring the solution will enable higher *C.D.*'s to be used before this condition sets in.*

Another aspect of the advantage to be obtained by bringing the depolarizer to the cathode is seen from a comparison of the reduction efficiencies of nitric acid at smooth and spongy copper cathodes quoted in Table LXVII, above. The surface of the latter is so much greater that there is greater opportunity for the reducible substance to be brought into contact with the cathode. For the same reason a platinized platinum electrode is more efficient, in spite of its low overvoltage, than other electrodes of higher overvoltage, e.g. smooth platinum, for the reduction of unsaturated acids and of phenol.†

* Elbs and Illig, *Z. Elektrochem.*, 1898, 5, 111; Goldschmidt, *ibid.*, 1900, 7, 263; Haber, *Z. physikal. Chem.*, 1900, 32, 193; Farup, *ibid.*, 1906, 54, 231; see also Akerberg, *Z. anorg. Chem.*, 1902, 31, 161.

† Russ, *Z. physikal. Chem.*, 1903, 44, 641; Petersen, *Z. Elektrochem.*, 1905, 11, 549; Fokin, *ibid.*, 1906, 12, 749; Fichter *et al.*, *Ber.*, 1914,

Temperature—Increase of temperature (a) lowers overvoltage; (b) increases the rate of reaction between hydrogen and depolarizer; and (c) increases the rate of diffusion of the depolarizer to the cathode. The actual influence on the electrolytic reduction is a balance of the effects of these three factors. If the reduction process does not require too high an overvoltage, increase of temperature would be expected to favour the improvement of the yield of reduction product; * if, on the other hand, the process requires a high negative potential, such as can only be obtained with lead or mercury cathodes at low temperatures, an increase of temperature will result in a decreased reduction efficiency. If an intermediate stage of reduction at a lower cathode potential is possible it will occur almost exclusively if the temperature is raised.† Variation of temperature thus offers an alternative method for altering the cathode potential of a given electrode in order to influence the reduction process.‡

Catalysts—Certain substances when added to the electrolyte produce an intensification of the electrolytic reduction process and increase its velocity; such catalysts are of two types. The first consists of salts of high overvoltage metals, from which the metals themselves are deposited on the cathode; § the second type are salts of metals capable of existing in two stages of oxidation, e.g. titanium, vanadium and iron. Thus, titanous chloride is reduced at the cathode to the titanous salt; the latter reduces the organic compound and is itself oxidized back to the titanous condition. At the cathode this salt is again reduced, and so the process goes on continuously even though only a small amount of titanium salt be present.||

The nature of the electrolyte has an important influence on the products of electrolytic reduction processes. The alkalinity or acidity, for example, plays an important part in determining the nature of the substance obtained by reducing nitrobenzene electrolytically: in this case the effect is mainly due to the influence of the pH of the solution on various possible side reactions.** In

47, 2015; *Helv. Chim. Acta*, 1922, 5, 252; Bancroft and George, *Trans. Amer. Electrochem. Soc.*, 1930, 57, 399. For specially designed electrodes which promote intimate contact of the depolarizer with the electrode, see Knobel, *Ind. Eng. Chem.*, 1925, 17, 826; Baillod, *Helv. Chim. Acta*, 1927, 10, 487.

* Elbs and Illig, *loc. cit.* † Cf. Law, *J. Chem. Soc.*, 1907, 91, 748.

‡ For another aspect of the influence of temperature, see Kaufier, *Z. Elektrochem.*, 1907, 13, 633.

§ Elbs *et al.*, *ibid.*, 1901, 7, 589; 1903, 9, 428; Chilesotti, *ibid.*, 1901, 7, 768.

|| Fichter and Bernoulli, *ibid.*, 1907, 13, 310; Luther, *ibid.*, p. 437; Snowdon, *J. Physical. Chem.*, 1911, 15, 797; Farnau, *ibid.*, 1912, 16, 249.

** For full discussion, see Glasstone and Hickling, *op. cit.*, p. 200 *et seq.*

other instances, however, such as the reduction of aromatic aldehydes, the cause of the difference in behaviour of alkaline and acid solutions is not so obvious.* There is reason to believe that hydrogen overvoltage is often less in alkaline than in neutral or acid solutions,† and this may be the cause of the lower reduction efficiency in the former solution. The presence of alcohol, which may be used as solvent, also reduces overvoltage, and its influence must be taken into consideration when examining any electrolytic reduction process. On the other hand, in acetic acid as solvent overvoltages are said to be higher than in aqueous solutions, and the greater efficiency of reduction of benzophenone in the former medium has been attributed to this factor.‡

Electrolytic Oxidation—In general the factors influencing electrolytic reduction also affect the oxidation process; these will be considered briefly.

Nature of Electrode Material—Platinum and gold anodes, with the highest oxygen overvoltages, should be most efficient for electrolytic oxidation, whereas nickel and iron should be least effective. The results in Table LXVIII indicate the anodic efficiencies for the oxidation of an alkaline solution of sodium formate at a C.D. of 0.033 amp. per sq. cm.§

TABLE LXVIII

CURRENT EFFICIENCY FOR THE ANODIC OXIDATION OF SODIUM FORMATE SOLUTION

Anode Material.	Overtoltage.	Efficiency.
Palladium	. 0.25	97%
Platinum	. 0.43	95 „
Nickel .	. 0.13	45 „
Iron .	. 0.25	18 „

Although this is not the exact order of anodic overvoltage there is a rough parallelism; the difference in behaviour of iron and palladium, with the same overvoltage, is, however, very marked. The electrode material apparently exerts a specific catalytic effect; a similar influence is observed in the results given in Table LXIX

TABLE LXIX

CURRENT EFFICIENCY FOR THE OXIDATION OF OXALATE AND NITRITE

Anode Material.	Oxalate Solution.	Nitrite Solution.
Platinum. . . .	87 to 98%	11%
Palladium	Nil	96 „
Iron	Nil	4 „

* Kaufmann, *Z. Elektrochem.*, 1895, 2, 365; 1898, 4, 461; Law, *J. Chem. Soc.*, 1906, 89, 1512; 1907, 91, 748; 1911, 99, 1133.

† See Glasstone, *J. Chem. Soc.*, 1924, 125, 2414, 2646.

‡ Swann, *Trans. Amer. Electrochem. Soc.*, 1933, 64, 313.

§ Foerster, *Elektrochemie wässriger Lösungen*, 1922, p. 312.

for the current efficiencies in the oxidation of 2*N*-potassium oxalate and *N*-potassium nitrite.

It is certain that definite rules cannot be laid down concerning the oxidizing efficiency of an electrode, but as a rule platinum and lead dioxide are the most, and nickel the least, efficient. The latter metal and iron are particularly useful if the organic compound is liable to be oxidized completely to carbon dioxide and water at platinum. The improved efficiency of an anode of large surface is very marked; both oxalic acid and methyl alcohol may be oxidized more readily at platinized than at smooth platinum, in spite of the lower overvoltage at the former electrode.* It should be noted that the range of oxygen overvoltage (Table LXVI, p. 492) is in any case not very wide.

Anode Potential—A series of stable potentials is difficult to obtain, because the value generally rises rapidly from the low potential, at which the anode dissolves, to a high value for passivity and oxygen evolution. Since a platinum electrode is nearly always passive, however, it is possible to obtain, to some extent, graded potentials with an anode of this metal. Dony-Hénault † oxidized a sulphuric acid solution of ethyl alcohol, and obtained the results given in Table LXX.

TABLE LXX

OXIDATION OF ETHYL ALCOHOL AT A PLATINUM ANODE AT DIFFERENT POTENTIALS

C.D.	Anode Potential.	Acetaldehyde.	Acetic Acid.
0.012 amp./sq. cm.	0.93	99%	1%
0.025 ,,	0.95	85 ,,	15 ,,
0.06 ,,	1.5-1.7	39 ,,	61 ,,

The oxidizing vigour increases with increasing anode potential, and by suitable regulation acetaldehyde or acetic acid may be made the main product. Attempts have been made to vary the oxidizing efficiency of an anode by superimposing alternating current on to the direct polarizing current, but hitherto these have not met with appreciable success.‡

Temperature—Oxygen overvoltage is lowered more by an increase of temperature than is hydrogen overvoltage, but the oxidation velocity is increased so much as more than to compensate for this decrease. The current efficiency for the oxidation

* Foerster, *op. cit.*, p. 810; Elbs and Brunner, *Z. Elektrochem.*, 1900, 6, 604; Salzer, *ibid.*, 1902, 8, 893.

† *Ibid.*, 1900, 6, 533.

‡ Reitlinger, *ibid.*, 1914, 20, 261; Allmand and Puttick, *Trans. Faraday Soc.*, 1927, 23, 641.

of sodium formate at an iron anode is increased from 18 to over 30 per cent. as the temperature is raised from 16° to 75°.*

Catalysts—The electrolytic oxidation process may be aided by the addition of catalysts or 'oxygen carriers' added to the electrolyte. Cerium, vanadium, manganese and chromium compounds have been used as catalysts; their action is probably similar to that of catalysts in electrolytic reduction processes.† Small quantities of certain salts, e.g. fluorides,‡ appear to increase the oxidation efficiency; their action is not clear. The medium itself often has a marked effect; in alkaline solution an oxalate can be readily oxidized at an iridium anode although not at one of palladium, but in acid solution the behaviour is reversed.

Influence of Time—This factor was not considered in connection with electrolytic reduction, but it is of importance in anodic oxidation. The potential of an anode generally rises during the course of polarization, and so its oxidation efficiency may be expected to increase; this is frequently found to be the case.§ If the substance being oxidized is likely to be completely decomposed at a high anode potential, the yield of oxidized product will be decreased.

The subject of electrolytic reduction and oxidation is so considerable, that it is not possible to give here more than a mere survey: for further details and references to the literature the monograph by Glasstone and Hickling should be consulted.

* See Foerster, *op. cit.*, p. 816; also, *idem.*, *Z. physikal. Chem.*, 1909, 69, 236.

† For references to patent literature, see Glasstone and Hickling, *op. cit.*, p. 339.

‡ Müller (E.), *Z. Elektrochem.*, 1904, 10, 753, 776; Fichter *et al.*, *Helv. Chim. Acta*, 1918, 1, 297; 1919, 2, 3.

§ Müller (E.), *Z. Elektrochem.*, 1904, 10, 49; Foerster, *loc. cit.*

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